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THE KINETICS OF HETEROGENEOUS REACTIONS AND THEIR DEPENDENCE ON SURFACE AND AGITATION.

DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in
the Faculty of Pure Science,
Columbia University.

BY

J. H. CROWELL, B.A., M.S.

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DEDICATED

TO MY WIFE, WITHOUT WHOSE SYMPATHY,
CO-OPERATION AND SACRIFICES THIS WORK
WOULD NEVER HAVE BEEN POSSIBLE.

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THE KINETICS OF HETEROGENEOUS REACTIONS AND THEIR DEPENDENCE ON SURFACE AND AGITATION.

ABSTRACT.

This research had for its purposes a general investigation of the subject of agitation and the establishment of a basis which might serve for a quantitative comparison of different agitations. Since the velocity of a heterogeneous reaction is generally quite sensitive to the effect of agitation, its use was considered in this connection. However, in the use of a heterogeneous reaction for such a purpose, the surface effects are equally important and had, therefore, to be studied as a part of the original problem.

A theoretical derivation of a new law (the Cube Root Law) concerning the rate of change of surface with time was made and its experimental verification in a solid-liquid dissolution system was accomplished under various types of agitation. Its special cases were investigated and shown to apply under many different experimental conditions. The Noyes-Whitney law of dissolution was shown to be one of these special cases. It was found that the Cube Root Law was very general in its application, and a study of several other types of agitation systems was made e.g. the solid-gas and solid-liquid chemical systems.

The values of the calculated constants obtained from the operation of the law were found to be excellent criteria of the intensity of the agitation accompanying the reaction and could therefore be used in the study of agitation in general. A detailed investigation was then made of a solid-liquid dissolution system (salt-water) in which the effects of all the known variables were studied. This study yielded many important and practical facts and established the usability of this method for the investigation of agitation. The idea of standard agitations was proposed, developed and extensively employed throughout this study.

Following this, the proposed method was found suitable for the study of agitation in larger scale equipment and its practica-

bility for such a purpose was established by runs made on a semi-plant scale.

The use and application of this law are recommended as a new and valuable tool in the study of heterogeneous reactions involving surface and agitation.

INTRODUCTION.

Agitation, one of the most extensively used unit operations, has long been a source of much trouble for the chemist and chemical engineer on account of the great lack of knowledge concerning both its qualitative and quantitative aspects. In fact, it is even a difficult subject to talk about, because the terms that are used to describe it are so general in their application that anyone attempting to be specific soon encounters great difficulty. It is hoped that this research will lay the foundation for a more logical and practical method of attack. The problem, briefly stated, is "How is it possible to introduce a practical and numerical evaluation of the phenomena that are produced in a system undergoing agitation?"

THEORY.

Webster defines agitation as a state of being agitated or moved with a violent irregular action, a stirring up, disturbance of tranquility or a commotion. The important features in this definition are violence and irregularity.

Since the mind cannot conceive of agitation without the presence of matter, it must be one of the attributes of matter. Therefore, when the three states of matter are considered, six possible binary combinations are obtained, viz. solid-solid, liquid-liquid, gas-gas, solid-liquid, liquid-gas and solid-gas. In addition, the more complex solid-liquid-gas system could be considered, but in general, it will be found that a great many agitations are of the binary kind. This division is based upon a consideration of the uses of agitation in the industry, where the purposes for which it is applied, fall into the following classification:

1. To procure and maintain a more uniform distribution or mixing of the materials used, or to increase the rate at which this distribution is taking place.

2. To keep the distribution of chemicals undergoing a reaction or obtained in one, in a satisfactory condition so that undesirable side reactions are avoided while the main reaction proceeds in the direction desired.

3. To maintain a uniform distribution or elimination of heat, thereby preventing local overheating or overcooling.

4. To increase the specific surface by separating the phases into many smaller portions. Here, such terms as grinding and macerating, spraying and splashing, emulsification, dissolving, bubbling and frothing indicate what is meant.

5. To decrease the specific surface as in agglomeration, crystallization, condensation, centrifuging, precipitation and similar types of processes.

6. To allow transportation to take place without the undesired separation or settling out of the phases, as in the movement of suspensions and sludges through pipes.

Other classifications have been made by Wood, Whittemore and Badger,[1] Killefer[2] and Seymour.[3]

Any practical correlation that can be made concerning agitation in any or all of these systems is bound to possess many arbitrary features, in the same manner that most generalizations concerning matter possess arbitrary conditions which have been imposed usually in order to fit the particular state of matter being considered. In order that any criterion of agitation may be of value, it must handle the complexities of the situations where it is to be used, in a practical as well as a theoretical manner. The selection and testing of criteria that will meet these requirements has been one of the principal objects of this research.

MATHEMATICAL AND PHYSICAL RESEARCH.

In the modern kinetic theory of matter with all of its ramifications, there is found what is probably the highest achievement in the use of mathematics and physics as applied to motion and matter. This concerns the motion of elementary, molecular and sub-atomic particles more than it does of matter in the bulk. For rigid bodies, the system of mechanics founded by Newton gives a clear picture for nearly all purposes. In fluids (the word is

used to include both liquids and gases), the progress in the description of their motions en masse, has, for our purpose, not been very satisfactory. Practically every physicist and mathematician of note has, at some time or another, turned his attention to what is admittedly, one of the thorniest branches of applied mathematics—hydrodynamics. In recent years, a related branch of this subject which is concerned with gases, viz. aerodynamics, has become increasingly prominent on account of the strong commercial stimulus coming from the success of the aeroplane and dirigible.

As the subject of fluid motion bears the imprint of the work of so many of the foremost scientists, it is difficult to single out the most important researches, but the work of certain men seems to stand out a little more prominently. Before the time of Euler, Galileo (1640), Torricelli (1643), Pascal (1651) and D. Bernoulli (1738) had laid the foundation for our modern hydraulics. In 1685, Sir Isaac Newton, in his Principia had considered the resistance that fluids offered to the motion of bodies in them. However, the real foundation for the study of fluid motion was laid in 1755 when Euler obtained the set of equations which bear his name.[4] Five years later, Lagrange obtained a set of equivalent equations that presents another manner of describing the motion of a fluid.[5] From that time on, the theory of fluid motion was developed rapidly, especially in the first quarter of the nineteenth century when Cauchy and Poisson published their classical memoirs on the theory of waves and wave disturbances. Stokes, in 1845, worked out the important law on the velocity of falling spheres in viscous fluids which finds extended use in sedimentation processes. At about the same time Poiseuille established experimentally his law on the straight-line flow of viscous fluids. Reynolds in 1883 extended this principle to larger pipes and established the laws concerning critical velocities. These he defined as the velocities at which the character of the flow changed from smooth rectilinear to turbulent. In 1858, the study of rotational, vortex or eddy motion was begun by Helmholtz in an article which has attained classical importance.[6]

During their times, Lord Kelvin and Rayleigh were both prolific investigators in this field and established many important

theorems especially in the problems of stability, viscosity and vortex motion. Other prominent investigators were Thomson and Tait, Maxwell, Kirchhoff, Love, Greenhill, Larmor and Rankine. Of all this vast amount of material on the motion of fluids, there is little that has had any practical use. The reason for this lies in the fact that the equations of motion become hopelessly complex in the actual motion, where it is no longer possible to ignore the factors of viscosity, surface tension, compressibility, boundary shape and inertia. These factors are extremely important at the increased velocities that are present in the actual motion. The introduction of all of these effects tends toward the production of considerable eddy motion, irregularity and highly turbulent conditions which are just what is desired for agitation. Yet, turbulency is the chief outstanding difficulty in the whole subject of hydrodynamics.

Excepting the study of turbulent flow in pipes, the only studies[7] of the turbulent state have been on the stability of steady motion of a liquid between two coaxial cylinders. This was first investigated by Mallock in 1888 and later by G. I. Taylor in 1922. It was definitely shown by the latter, both theoretically and experimentally, that when the inner cylinder was fixed the steady motion was stable for all observed speeds of rotation. When the outer cylinder was fixed and the inner rotated, there was stability only at sufficiently low speeds of the inner one. In all cases, the speed at which the instability began was sharply defined. The similarity in the existence of a critical value for the velocity as in the case of rectilinear flow seems very encouraging. Coming still nearer to the actual motion, the study of the motion of a fluid in the neighborhood of a solid (a plane lamina) which moves in simple translation through the fluid at rest, shows that the motion is extremely complex and difficult to interpret.[8] However, in the case of two-dimensional flow of quite viscous liquids, it has been possible to photograph the lines of flow and in certain cases to show that the mathematical equations of motion are followed fairly closely.[8] For the actual three-dimensional turbulent motion in the general case, so far practically no progress has been made.[8] There has, however, been considerable experimental work done on the resistance of ships and on the pattern of flow of

water in the neighborhood of moving solids so that a good deal of qualitative information is available about this phase of the subject. With respect to the similarity of motion of liquids in geometrically similar boundaries but of different sizes or the question of scale, the work of Stanton of the National Physical Laboratory should be mentioned.[9] This brings in the whole question of Dynamical Similarity and the use of models in the study of fluid motion. The use of this method has been attended with considerable success especially in the study of surface waves, ship resistance, aerofoils and the flow of different fluids in pipes of different diameters. An excellent exposition of this important theory has been given by A. H. Gibson.[10]

In concluding this resume, a word from Lamb (an eminent authority on this subject) is not out of place at this point. He says, in speaking of the problem of steady viscous fluid motion, that, ". . . although the equations of motion of viscous fluids are well established, the calculations based on them are often subject to serious limitations. . . even when the investigations are rigorous the types of motion obtained are often unstable." [11] Again, in speaking of turbulent motion, he says, "It has been seen repeatedly that unless the velocities involved are exceedingly small, or the spatial relations very constricted, calculations based on the hypothesis of rectilinear flow, . . lead to results which are in striking disaccord with experience. What really happens is that eddies are formed, with the result that there is an interchange of momentum between adjacent layers of fluid . . . and we are now concerned with the momentum of elementary portions of fluid regarded as continuous." [11]

PROPOSED METHOD OF STUDY

From the foregoing it would seem that a direct mathematical attack upon the problem is precluded. What is needed is a new type of approach—some method whereby the effect of the motion is the thing considered or some way in which the total mechanically-integrated effect of all the small, irregular motions is automatically taken care of by the method or substance itself. This would avoid the difficulties involved in attempting to specify the

motion, point by point throughout the system from moment to moment. This requires that some measurable property or effect of the agitation be taken as a basis for the indirect evaluation of the agitation itself. This property or effect can best be disclosed by the introduction of another phase to form one of the agitation systems referred to, so that the cumulative effect of the agitation will be made apparent by its action on the added substance or phase. This added substance can be called the indicating substance (I.S.). If the various purposes for which agitation is used are studied, it may be seen that there are many effects which could be used to measure its efficiency in serving its purpose. For example, the following criteria might be employed: the rate of mixing of solids, the uniformity of heat distribution, the rate of solution or sublimation of a solid, etc. As this method involves the selection of arbitrary standards, absolute values would, of course, not be obtained.

For this research the binary combination chosen for study was the solid-liquid system, utilizing the rate of dissolution* of a solid (I.S.) in a liquid under agitation as the criterion or measure of that agitation. The reasons for the choice of this system are first, its application in industry should be relatively less difficult than the other systems and second, any results obtained should be of immediate practical value. However, this choice involves a serious complexity due to the simultaneous rate of change of surface during the dissolution. This, of course, applies only to the general case where the surface is allowed to vary. Since these two subjects, agitation and surface effect, are the two characteristically inherent properties involved in the velocity of a heterogeneous reaction, one is thus led, in the general case, from a study of agitation to a study of the kinetics of surface change at the same time.

While the discussion so far has purposely been very general, it must be realized that the field is entirely too large for the application of the broad idea to be applied in a detailed manner to all systems at this time. All that can be expected is that enough

* The word "dissolution" will be used throughout this dissertation to indicate the process of dissolving or of forming a solution.

will be shown of its application in the solid-liquid system and to a limited extent in one or two of the others so that some inference may be drawn concerning its general applicability. The discussion will therefore, from this point center mainly on the properties of the system chosen and will only incidentally consider other systems as the opportunities may be presented.

PREVIOUS WORK ON AGITATION.

The literature on this subject is extremely meager and nearly all the research has been but indirectly connected with agitation, as such. On the subject of stirrer efficiency, an article by Wood, Whittemore and Badger[1] published in 1922, seems to be the first practical study made upon the problem* They measured the rate at which the mixing of a strong salt solution and a supernatant water layer took place under different stirrer speeds. They used an ordinary paddle agitator in a 600 gal. wooden tank. The distribution of the salt was determined at various fixed points by means of electrical conductivity methods. The time necessary to obtain complete mixing was used as the comparative element. They showed that complete mixing took place very rapidly and usually around one minute under the conditions which they operated. They also called attention to the fact that an ordinary paddle agitator was much more efficient than was usually thought. Moreover, they showed that the visual appearance of the motion and the power consumption were unreliable and unsatisfactory as gauges of the efficiency of the stirrer. They also tried several chemical methods which they reported as unsatisfactory. Certain other features of their work will be discussed later. Studies on the rate of solution of crystals were said to be under way, but up to the present time no further published articles on this subject have been encountered.

The statement concerning the efficiency of the paddle agitator was confirmed by Hill in 1923, in connection with observations on the rapid rate of solution of a dye, as shown by samples of a solid (which absorbed the dissolved dye) taken at different times after the addition of the solid dye.[12]

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* See also, the reference to Jablczynski.[23]

E. V. Murphee[13] in 1923, considered the rate of solution of crystals and worked out a mathematical formula based upon the change in linear dimensions of the average crystal during the progress of solution. He considered that with certain variations it might be used to test the relative agitation efficiencies of different types of equipment. An experimental laboratory run on the solution of potassium dichromate crystals was presented in support of the equation but there was no general investigation of the subject and the introduction of the linear dimension of the crystal led to a somewhat complex formula and lack of freedom in treatment. This work will also be referred to again under the study of surface effect.

In 1924, W. A. Roth [14] used a semi-quantitative solution method to test the suitability of a stirrer for use in calorimetry. He used a crystal of potassium permanganate imbedded in a soluble colorless salt which was fastened to the stirrer and noted the rate of solution from the time at which the streaks of color began to appear. He states that the use of the heat of solution effect could not be used as a criterion on account of the small volume of the solution employed.

From the physical standpoint, Dodd in 1927,[15] published a method of comparing the times of complete mixing of two liquids by determining the time required to make the striations due to density differences disappear, while the entire system was being agitated. He used gasoline and carbon disulfide, also strong salt solution and water as the agitation systems for the study. He reported, after an intensive study of the problem, that the time of complete mixing depends on the rate of stirring, position of the stirrer, shape of the vessel, etc., but did not consider these variables any further. The point of disappearance was quite abrupt. This contribution is a study of a rather specific case of agitation and it is doubtful if the method would have much general application.

Where the effect of agitation upon the velocity of a strictly chemical reaction is concerned, the work of Reid and his students is quite important.[16, 17] They studied a variety of systems (in the sense that the word is herein used) and found that among the chemical reactions studied there were three classes, first, those in

which the rate of reaction is approximately a linear function of the stirring speed, second, those in which this function is linear only after a certain speed of stirring is reached and third, those whose rates are independent of the stirring speed. In the first class they found the following reactions: the ethylation of benzene by ethylene, the oxidation of sodium arsenite by oxygen, the oxidation of p-nitrotoluene by chromate mixture and the reduction of nitrobenzene by iron and dilute acid. In the second class, they placed the catalytic hydrogenation of cottonseed oil and of a hydrocarbon. In class three, a typical reaction was the saponification of ethyl benzoate at 60° C.

Under the conditions that they used they stated that their results could be expressed in the following formulae:

Class one. $V = a + br.$

Class two. $V = b'(r - r').$

In these formulae, r is the stirring rate in thousands of r.p.m.; V is the reaction velocity, usually expressed in loss of weight in g./cm^2/sec. or volume of gas absorbed per mol per sec.; a is the velocity when there is no stirring; r′ is the rate of stirring at which the linear part of the curve would cut the rate axis if prolonged, while b and b′ are constants. The speeds were all relatively high, i. e., from three thousand to thirteen thousand r.p.m. Their agitators were of the Witt disc type[18] and the exact shape used varied, depending on whether solid-liquid or gas-liquid systems were being studied. The vessel was provided with several large baffles so that it is justifiable to assume that a high degree of agitation must have been obtained. Beyond the reactions studied or the ranges of stirring rates they employed, they did not consider the effects of the many other variables. In particular, the methods used were such as to eliminate any appreciable change in composition throughout the separate runs with the given speeds and to keep such changes, when they were unavoidable, as nearly constant in value as possible. Whether these linear relationships would hold for example, with differently shaped agitators, placed differently, is problematical. It is quite likely that the form which the function assumes in these reactions depends on many other things than the stirring speeds even if it is assumed that the

velocity of the reaction is always measured under the same conditions of concentration and surface.

It can be seen that the application of any of these reactions to industrial work in an endeavor to use them as measures of the commoner rates of agitation which are found in industry, would require considerable change, especially in the range of relatively slow rates. The authors were not concerned with these possibilities.

In other work in which there have been attempts to relate the speed of stirring to the velocity of the action studied, the results are at such variance that a generalization is made only with difficulty and is of doubtful value. Most of these relationships are the results of studies widely differing from each other in the many conditions that accompany the reaction studied. With no restrictions on the shape and dimensions of the agitator or of the vessel used (for example), one cannot expect an agreement between different investigators concerning the influence, for instance, of doubled r.p.m. even on the same reaction.

In general, the velocity of the reaction when run under identical conditions except with a different stirring rate, is found to vary as some power of the stirring speed expressed as r.p.m. Mathematically stated, $V \alpha (n)^x$, where V is the velocity, n is the r.p.m. and x is a number, usually fractional and less than unity. The values of x reported by different authors range from 0 to the more usual values of ⅔, ½, ⅘ and 1, depending on whatever value seems to fit their particular choice of reaction or set of conditions best.[19, 20, 21, 22]

Another formula which is closely related to the one just given was published by Jablczynski in 1908.[23] It has the following form: $K_1/K_2 = (n_1/n_2)^x$ where the (K)s are the values of the velocity constants at their respective stirring speeds and x has the same significance as before. He also calls attention to the variance of x with the change of apparatus. This formula has been found satisfactory by a number of investigators for the ranges of stirring speeds and the conditions and reactions that they employed.[24] The variation of x in the same reaction when the range of stirring speed was taken large enough to dis-

close it was shown by Huber and Reid's Class two reactions (l.c.) and also by v.Wolff.[25] The change in the character of the agitation as the stirring rate was increased must be the cause of the change in the form of the functional relationship between the velocity and the stirring speed. As the forces producing the motion change due to the increasing r.p.m., their relative intensities change also and certain components become more predominant. The result is that the total characteristic effect upon the reaction velocity appears in a new role. This difference is strikingly evident when one considers the change in character of the agitation produced when a ball mill, centrifuge or an impeller agitator is run below or above its proper speed. These effects of change in character of the agitation appear only if the reaction velocity is sufficiently sensitive towards agitation within the range of stirring speeds that has been chosen. Considered in this light, it can be seen why the relationship between velocity and stirrer rate has appeared in so many different forms, depending on the reaction, its degree of completion, range of speeds and other conditions imposed. Moreover, there should be, a considerable difference (for instance), between those reactions where a gas is evolved at the surface of the solid and those where the reaction seems to be merely that of pure solution without such a complication being present. Such a difference might be due to the agitation caused by the gas evolution and its surface-covering effect, both of which should have some effect upon the form of the relationship between the stirring rate and the reaction velocity. It is the agitation and the surface change that affect the reaction rate to the greatest extent in most cases and the r.p.m. of the stirrer is only one of the many factors that bear on these two influences. It is obvious that the stirrer rate i. e., the r.p.m., is only chosen for the place of prominence in the formulae due to the ease and simplicity of its numerical designation.

In this research an endeavor has been made to visualize the problem as a whole and to bring together and coordinate all of the known essential factors.

GENERAL QUALITATIVE CHARACTERISTICS OF AGITATION.

Nature of Agitation. When a medium, a liquid for example, undergoing a visible agitation is inspected, the following characteristics are noted:

1. The contiguous portions undergo displacements or relative changes of position with respect to each other which vary in magnitude and direction.

2. The rates at which these displacements occur are different for different points in the medium, e.g. some portions may seem to move almost as if they were rigid bodies.

3. The continued application of forces is necessary to generate and maintain the motions developed.

4. When the distribution of the forces existing in the fluid is investigated, it is found that their intensities and directions vary from point to point.

5. Numerous local centers of disturbance, eddies, whirlpools, splashes and irregularities of all description form and disappear.

The magnitude, randomness of direction, rate of completion and frequency of occurence of these relative displacements are the fundamentally distinctive properties of our concept of agitation and any operation or change whereby any of these properties is affected has an effect upon the intensity and character of the agitation.

These are descriptive terms applied to the action occurring at discontinuously located spots or regions in the main body of the liquid. Therefore, even if it were possible to obtain a complete knowledge concerning any one of these spots, the agitation of the total volume of the liquid as a continuous medium would still be impossible to calculate. We can, however, still think and speak of the agitation of the fluid or liquid en masse, as an ensemble of all these local centers of turbulence, but its evaluation in this sense can be done only by some physical method as outlined in the proposed method of study.

This manner of flow or mode of motion in a liquid has been

termed by Lord Kelvin, the "turbulent mode" and is, as herein postulated, the chief underlying characteristic of all agitation. The degree of this turbulence is a measure of the intensity of the agitation in any particular example of a medium that is being considered. One might define agitation as that mode of motion, which being imparted to a medium, is characterized by the production of turbulence.*

Intensity of Agitation. In the conception of agitation here formulated, intensity may be considered as an ordered magnitude and it should be possible to arrange a series of agitations in order of their increasing degrees of turbulence. It would not, of course, be a quantity. Therefore it would not be additive in the sense that if two equal systems having equal intensities of agitation were added together, the resulting system would then have twice the intensity of agitation that each system had singly. In this, it resembles the idea of temperature. Among the implications of this idea of a scale of intensities, is that of comparison, so that one could speak of comparing two agitations (the operations in bulk) by comparing their relative degrees of turbulence. Accordingly, two agitations equal in intensity to a third would be equal in intensity to each other. Hereafter in this dissertation, in any mention of comparison of agitations, it should be understood that it will be in this sense. It is also well to point out that no postulates have been made about the *quantity* of agitation, if such a thing exists. Moreover, while the idea has so far been restricted to agitation produced by mechanical means, there is no theoretical reason why molecular and thermal agitations, such as are found in diffusion, could not be included in a still more generalized idea of agitation, but this aspect will not be gone into further.

A more important question is that of the determination of the relative position of the intensity of a given agitation in such a scale. In accordance with this idea, the one having the greater

* There is no well-accepted theory concerning the nature of the motions involved in turbulence, but most writers seem to think of it as some sort of a combined shearing and eddying motion superimposed upon the ordinary laminar flow.[26]

turbulence has the higher intensity of agitation. In many cases, this difference is great enough so that a rough approximation can be made from appearances alone. But, as Wood, Whittemore and Badger have pointed out, this is quite deceptive, so that not much reliance can be placed upon it as a method of comparison unless the differences are very great.

In any event, methods based upon the addition of another substance can be used in the manner referred to in the previous pages. The turbulent motions of the medium may be used to perform work of distribution on the added substance. For instance, in an immiscible liquid-liquid system, the entire volume of the container could be subdivided into regions and the analysis of a sample which had been withdrawn from each region would indicate the extent of distribution or mixing that was present in that region. If this extent now is given a numerical value based upon complete uniformity (e.g. if the basis were taken for complete uniform distribution to equal 100), a mean or average value of the intensity of the entire volume could be computed from an arithmetical summation of all the values of the smaller component regions. Such a system (oil-water) was investigated in this laboratory several years ago and appeared to offer considerable promise.[27]

Another and better way would be, as mentioned before, to add an indicating substance to the medium so that its distribution is an automatic result of the combined effect of all the small motions and expenditures of energy throughout the entire volume. Then, regardless of their local variations, the measure of the mean value of the intensity of the agitation as a whole in the entire volume, would consist in a measure of the rate and thoroughness with which this distribution progressed. If a system at one agitation performed a given distribution in a less time than it did at a different agitation, the former is more intense than the latter. If the numerical value of the work involved in the distribution were known or calculable, an absolute measure of the intensity could be obtained. Not knowing this work, we still have a relative measure of the intensities provided we give each system the same amount of distributive work to perform. This last postulate forms the basis of the experimen-

tal comparison of agitations considered in this research. For example, two solid-liquid systems differing only in one particular variable (say the length of the agitator) are given the same amount of distributive work to perform, viz. the dissolution and distribution of the same amount of the same solid. Then, the rates at which they perform this amount of work are compared and the one completing this work at the faster rate or in the shorter time, is considered, by definition to have the higher average or mean intensity of agitation.

The next section will consider the specific factors that influence the rate at which the distributive work is performed in a solid-liquid system where the solid is soluble and the work of dissolution is part of the total work of distribution. In the experimental part most of the work was carried out using granular salt (NaCl) as the solid and water as the liquid.

SPECIFIC FACTORS AFFECTING THE RATE OF DISSOLUTION AND DISTRIBUTION IN A SOLUBLE SOLID-LIQUID SYSTEM.

1. Those concerning the solid.

The rate at which a given mass of a solid dissolves in a liquid depends on the following factors, other things being equal.

(a) The specific surface of the particles of the solid or their average surface per unit of weight.

(b) The uniformity of distribution in size throughout the particles.

(c) The shape characteristics of the particles determine the specific surface, in that as they approach those of a sphere the specific surface approaches a minimum. Therefore, for fast rates, the particles should be as angular, sharp and jagged as possible.

(d) If the particles are not homogeneous or if their nature varies from one to the other, the rate of dissolution will vary also. If the material in each particle is anisotropic, but is not regularly crystalline, the separate differences in rate of solution from each face will disappear and the total rate will be a com-

posite of the single rates. If, however, the individual faces of a crystal are compared then these differences are revealed.[28]

(e) The diffusion coefficient of the dissolved solid in the given liquid. Other things being equal, the rates of solution of two different solids in the same liquid will vary directly as their diffusion coefficients.

(f) Other influencing factors are such things as, incipient fractures, dust, gas films, agglomerates, density currents and convection streams.[29] When a material has been crushed or shattered by a blow, the presence of cracks and incipient fractures is generally quite apparent and interferes with the use of the method as a means of the determination of the relative surfaces of powders.

2. Those concerning the liquid.

(a) The agitation of the liquid in contact with the surface of the solid. Regardless of whether or not there is a skin layer of slow-moving or stationary liquid immediately adjacent to the solid surface, the agitation of the liquid which is next to this layer or the surface is the most important factor in the rate of solution of the solid.

(b) The temperature affects the rate of solution in two ways; it changes the solubility, thus increasing the distance necessary to pass through to arrive at equilibrium and it increases the actual velocity itself through its kinetic influence upon the diffusion rate. The temperature coefficient is considerably less than that of homogeneous reactions.[30]

(c) The concentration of the dissolved solid already in solution. This very important effect will be discussed in more detail later. Its general influence is to decrease the rate of solution.

(d) The viscosity of the liquid. This affects the rate of diffusion and is frequently the governing factor in the power-agitation relation. The coefficient of viscosity is the ratio of the shearing stresses in a moving liquid to the rate of shear undergone by the liquid.

3. Those concerning both liquid and solid.

(a) The chemical nature of the two. By this is meant their solubility, whether they react chemically or not, the nature of the reaction and the nature of the products if they do react. For example, a coating of an insoluble protective nature may be formed on the surface of the solid or a gas may be formed whose escape causes an increased agitation or a chemical reaction may have to take place before solution is possible.

(b) The relative density relationships of the solid, liquid and solution will have something to do with the rate of solution.

(c) The proportion of solid and solvent governs the amount of total interfacial contact surface presented and, other things being equal, the rate varies with the total surface between the phases.

4. Distribution.

By this term is meant the locational placement of the solid in the final form which it attains. It includes the processes of dissolution and transportation to give a final uniform concentration throughout the liquid, but in general, it does not imply anything other than the idea of transportation.

(a) The average intensity of agitation of the liquid bulk as differentiated from that of the liquid in immediate contact with the surface of the solid.

(b) The uniformity of agitation throughout the liquid affects the rate at which the thoroughness of distribution is obtained.

SPECIFIC FACTORS AFFECTING THE AGITATION ITSELF.

1. Type of generating motion.

Under this head can be listed certain prominent types, characteristic of the manner in which the motion is imparted to the liquid in order to produce the agitation. It is hardly necessary to say that there is a very great variation in the agitation produced by the same amount of force depending upon the manner in which this force is applied.

(a) Free Rotational.—Aside from the friction of the circular container walls and bottom and the viscosity of the liquid itself, there are no other surfaces to impede the rotational motion. Illustration—a simple straight paddle agitator rotated with uniform speed in a smooth cylindrical vessel.

(b) Impeded Rotational.—The same as (a) but containing breakers or baffles of any type which offer resistance to the general rotational trend. The common type of industrial agitation is usually this type with some modification of the agitator.

(c) Tumbler Motion.—Such as would be obtained by rotating a closed barrel about a horizontal axis perpendicular to its length.

(d) Shaker Motion.—Like that obtained in the ordinary form of bottle shakers found in the laboratory. A jerky back-and-forth motion.

(e) Ball Mill Motion.—Such as is obtained in a cylinder lying horizontally and rotated about its longitudinal axis, e.g. a ball mill.

(f) Pulsating Motion.—Obtained (for example) when a perforated piston moves alternately back and forth through a liquid as in various kinds of pulsating jigs.

(g) Straight Line or Unidirectional.—Such as the flow of a river or canal under gravity.

(h) Random Motion.—The motion is more or less random, for instance that caused by irregularly-placed air jets in a liquid would be somewhat random.

Combinations of all these motions are extensively employed in industrial plants on account of the ease with which a modification of the character of the agitation is obtained. This classification is arbitrary and does not pretend to be complete as the subject does not lend itself to a detailed analysis in this manner. For a classification of different types of agitators see Killefer's article.[2]

2. Shape of the container.

This is a matter of much importance as it serves in general

to modify the generating motion and may act in many different ways to alter the applied force and to affect the distribution.

3. Type of impeding or deflecting walls or barriers.

This is the question of baffles and breakers and is the most often used and most easily operated device for the transformation of pure translational or rotational motion into agitation.

4. Total volume of the system.

The amount of free space in the container available for motion and the relative proportion of the solid and liquid as parts of the total volume of the system must be considered.

5. The generating forces.

The questions as to where and how the motive forces are to be applied in each case and the resulting effects of momentum, inertia, power requirements, materials strength, etc., are largely those of machine design. It is sufficient to say that the effect of change in the points and manner of application are immediately evident in the intensity and character of the agitation produced.

6. Regimes under different intensities of generating forces.

The changes in the character of the agitation have been mentioned before but are here emphasized again.

7. Degree of magnification.

This is again the idea of Dynamical Similarity which was mentioned before. It is evident that even if two systems were geometrically similar and on a different scale, they could still be dynamically dissimilar. This is an entirely too large a problem to be treated in this work.

SURFACE EFFECT AND THE CUBE ROOT LAW.

This section will consider the rate at which the dissolution of a solid takes place in a liquid, the known laws and the derivation of a general law.

1. Fick's Law of Diffusion.

The law concerning the rate at which a dissolved substance

diffused in solution was enunciated by Fick in 1855[31] and is a special case of the more general law known as Fourier's Law of Linear Diffusion which was discovered still earlier in 1822. Beyond stating how the law operates and its connection with the problem in hand, it will not be necessary to consider it in detail. One way of stating the law is to say that the quantity of solute (ds) which diffuses through an area A in a time (dt), when the concentration changes by an amount (dc) through a distance (dx) at right angles to the plane of A is given by the expression $ds/dt = -DA\,dc/dx$.

In other words, the coefficient of diffusion D is the amount of solute which will cross one square centimeter of cross section in one unit of time if the change in concentration per centimeter in a direction perpendicular to this cross section is unity.

Several things should be mentioned about this equation and the assumptions that are implied in it. All other motions except that of the molecular agitation itself are rigorously excluded and the system is kept at constant temperature and absolutely still. The law is here stated for linear diffusion only, i. e., the diffusion takes place in but one direction. The experimental proof is based on the diffusion taking place linearly upward against the force of gravity which interferes seriously when attempts are made to study it in three dimensions.

Further, Weber has shown that the diffusion constant decreases as the concentration rises.[32] Also, it concerns the process of diffusion of a salt after it is in solution and not the process by which it dissolves before it is in a position to diffuse. Diffusion itself, is a slow process but it takes only a small amount of stirring to promote the distribution so greatly that but a few moments are required to reach a uniform concentration which otherwise would need years to complete. This is because stirring takes those layers which at the start had relatively small interfacial contact area with the less concentrated solution and low concentration gradients and stretches them out into very thin convoluted strata with great contact areas and high concentration gradients. The result is that the forces of diffusion under these conditions are enabled to establish equilibrium very rapidly and reach a uni-

form state of distribution. One notes again, the characteristic role that increased specific surface plays in this process.

The rate of diffusion is thus seen as playing an important part in the distribution and in the equalization of concentration when agitation is present and also as the governing rate of distribution when there is no agitation. There are also certain reasons for postulating that it may be the governing rate even in those cases where there is agitation but these will be considered in the next section.

2. The Noyes-Whitney Law.

This law concerns the rate at which solids dissolve in their own solutions.[33] The authors used two slightly soluble compounds for their work, viz., benzoic acid and lead chloride. These materials were cast in the form of cylindrical sticks on glass cores and after insertion into wide-mouthed bottles containing water were rotated at a constant rate in a thermostat for a given length of time. Analysis of the solution then gave the amount that had dissolved. The run was then repeated, using the same stick with fresh water, but for a longer time. In this way, the amounts dissolved in ten, thirty and sixty minutes were obtained. The law which these results supported quite well may be stated thus:

The rate of concentration change (here equal to the rate of dissolution) at any instant is directly proportional to the difference between the concentration of a saturated solution (C_s) and the concentration (c) existing in the solution at that instant, or mathematically,

$$dc/dt = k(C_s - c) \text{ or } kt = \ln(C_s - C_o) - \ln(C_s - c).$$

Due to the slight amount of the solid dissolved, the surface change of the cylinder was considered to be negligible. Similarly, the concentration was assumed to be uniform throughout the solution. They explained the action on the assumption that a very thin layer of saturated solution was formed at the surface of the solid and that the rate at which the solid dissolved was governed by the rate of diffusion from this saturated layer into the main body of the solution. The thickness of this layer was determined by the intensity of the agitation.

A few years later, L. Brunner and Tolloczsko in a series of experiments modified the method and extended the range of substances studied to include more soluble compounds. They also showed that the law held under a straight-line flow type of agitation as well as a rotational type and used a range of r.p.m. in the latter which ran from 440 to 2,300. They also used initially different concentrations of solution and solids of known area in different volumes of liquid. They showed that the value of the constant k depended on the surface exposed, the rate of stirring (or water velocity across the surface), temperature, structure of the surface and the arrangement of the apparatus.[34]

Following the work of these two, E. Brunner, working in Nernst's laboratory, studied the problem still further in an effort to establish a definite numerical connection between the constants obtained and the diffusion coefficient of the dissolving solid.[35] He gave values which he had calculated for the thickness of the postulated layer of saturated solution on the surface of the solid. Simultaneously with the above publication, Nernst advanced a theoretical generalization of the law to include all kinds of heterogeneous reactions, postulating that at the boundary surface of the different phases, the equilibrium is set up at a practically instantaneous velocity compared with the rate of diffusion and emphasized further the idea of the adhering layer.[36] According to these ideas the velocity of a heterogeneous reaction was determined by the velocities of the diffusion processes that accompanied it.

Numerous other investigators have reported evidence in favor of the Noyes-Whitney law in various kinds of reactions.[37]

Certain cases have also been reported where the law does not hold, such as the dissolution of arsenic trioxide in dilute sulfuric acid and the solution of certain metals in acids, e.g. zinc in sulfuric acid.[38] Among the interfering actions which are considered to be the cause of deviation from the law, may be mentioned: the slowness of the chemical reaction at the surface of the solid, the action of local elements as in the case of metals, the periodic nature of some of the reactions and the fact that some reactions require an induction period before they start. Other interfering

actions are the presence of passive layers and the evolution of gas bubbles which may act either to protect the surface or to cause additional agitation as they escape from the surface into the liquid.[38, 39]

Where a chemical reaction is taking place simultaneously as in the above examples and especially where its velocity is slow compared to the rate of diffusion, the resultant overall velocity is supposed to be ruled by the rate at which the chemical change takes place. In this event, increased agitation has little effect and the temperature coefficient is relatively large.[40] On the other hand, if the chemical reaction is fast compared to the rate of diffusion, the resultant overall velocity will be ruled by the diffusion rate, in which event, increasing the agitation will have a considerable effect but the temperature coefficient will be small. Neither has the law been found to apply very satisfactorily to the rate of crystallization,[41] as would be expected, although even in this there has been some disagreement.[42]

From the descriptive standpoint, the rate of solution has been studied by Schurr[28] and his work includes some excellent photographic evidence of the manner in which the actual regimes of action are set up around the surface of the solid.

The theory as outlined by Nernst emphasizing the diffusional character of the process and postulating the existence of such a layer, has been the target of some rather serious criticism, both from the theoretical and experimental standpoints. First, it was questioned on the basis of the unlikelihood of occurrence of such extremely rapid rates of attainment of equilibrium at the crystal face as are required by the hypothesis and second, on the lack of definite proof of the fact that such a layer really exists. Wilderman, in particular,[43] subjected the entire Nernst-Brunner theory of the layer to a most severe analysis and experimental study and threw considerable doubt upon the diffusional nature of the entire process. Also, when the process of dissolution is considered in connection with the other heterogeneous systems and reactions such as sublimation, evaporation, etc., there is some hesitancy as to the acceptance of the preponderant role that diffusion is supposed to play.[44] Lastly, among some of the more recent investi-

gations, that of the solution of metals in acids, shows that even if the diffusion theory is correct, that the question of which shall play the primary part, diffusion rate or chemical reaction rate, is one of choice of the attendant conditions and thus is not inherently related to the nature of dissolution.[45]

In conclusion, it can be said that the law in its original form without any assumptions regarding the mechanism by which the process takes place, has been quite generally substantiated by experiment.

Regarding the surface effect under conditions of constant volume and agitation, all of the work has been done with the surface kept constant or its value has been known and the rate calculated per unit of area. In no case that we have been able to find, has it been incorporated into the law as a variable and allowed to change as such without control during the course of the reaction.* In a few instances of crystallization studies, attempts have been made to correct for the change of surface from time to time during the reaction, whenever the changing surface area affected the rate of the action in a material manner.[46]

In any event, whether the velocity of the chemical reaction or the rate of diffusion determines the resultant rate of the combined process of transformation of the solid into its dissolved and distributed products, the three outstanding factors are concentration, surface and agitation. Of these three, the concentration has obviously presented few difficulties in measurement and is more or less a controllable factor compared with the other two. Except where the solid surface presented to the action of the liquid is plane, there is a constant change in its area and thereby a slowing down of the rate of dissolution, for it is almost an axiom in chemical philosophy that the rate of chemical action is, ceteris paribus, directly proportional to the surface exposed to that action.

In the next section a law will be derived in which the velocity will be related to the concentration and the surface, the latter entering as a fundamental variable and for which no correction is necessary.

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* For an exception to this statement see p. 71.

If the relationship between velocity (V), concentration (c), surface (s) and agitation (a), be written symbolically as $V = F(c, s, a)$, where (F) is the general unknown function that would apply when all other variables are held constant, it can be seen how much progress has been made in solving the most general problem. If it is admitted that the previous attempts to relate velocity to stirrer speed have been successful, then we may regard (V) as having been expressed as a function of (a) and in the Noyes-Whitney Law we may consider (V) as expressed as a function of (c). The derived law, on the other hand expresses (V) as a function of both (c) and (s) and therefore, will, as shall be seen, contain as special cases, relationships of the velocity with surface and with concentration (i. e., the N. W. Law).

3. The Derivation of the Cube Root Law.

(a) The General Case.

After the mathematical expression for the law has been derived, its properties and implications will be discussed.

Let w_0 = the weight of the crystal at the start or when the time t=O.

Let w = the weight of the crystal at time t.

Let w_s = the weight of solid needed to saturate the liquid under the given conditions of temperature, volume, etc., at the start.

Let S = the surface of the crystal at the time t.

Let V = the volume of the solution and (d) the density of the crystal.

Then dw/dt will be the rate of change of weight or the velocity of solution of the crystal and if we assume in accordance with custom, that it varies directly as the interfacial area of contact surface together with the difference between the concentration at saturation and the existing concentration, all taken at the same instant of time, we have

Eq. (1). $dw/dt = -K_2S(C_s - c)$.

In this equation, K_2 is a positive constant, (c) is the concentration of the solution at time (t) and (C_s), its concentration at saturation but (S) is no longer a constant.

Now $w_0 - w$ is the weight of the crystal that has dissolved up to the time (t) and $(w_0 - w)/V = c$, if (c) equals zero when (t) equals zero. Similarly, $w_s/V = C_s$. Substituting these values in Eq. (1) gives

Eq. (2). $\quad V(dw/dt) = -K_2S(w_s - w_0 + w).$

Also provided there is no change in shape as the crystal dissolves (a point which will be discussed fully later), its surface varies as the two-thirds power of its volume*, or $S \alpha v^{\frac{2}{3}}$ or, since $w/d = v$ then $S = k_s w^{\frac{2}{3}}$, where (k_s) may be considered as containing a shape constant whose value would depend on the shape of the crystal.

Substituting for (S) in Eq. (2) and setting $w_s - w_0 = g$, (for convenience) we obtain the following equation where (K_1) is a combined constant.

Eq. (3). $\quad V(dw/dt) = -K_1 w^{\frac{2}{3}}(g + w).$

On rearranging, the following integral is obtained.

$$V \int \frac{dw}{g w^{\frac{2}{3}} + w^{\frac{5}{3}}} = -K_1 \int dt + C, \quad C = \text{Integration Constant.}$$

After letting $g^{\frac{1}{3}} = a$; $w_0^{\frac{1}{3}} = b$ and $w^{\frac{1}{3}} = x$ and knowing that when $t = O$, $w = w_0$ and $c = O$ (here), we obtain the equation for the general case where the initial weight taken is either greater than or less than, but not equal to the amount needed for saturation, or $w_0 = w_s$.

$$\text{Eq. (4).} \quad K_1 * t = \frac{V}{a^2}\left(\sqrt{3}\tan^{-1}\frac{2\sqrt{3}\,a(b-x)}{3a^2 + (2b-a)(2x-a)} + 1.1513 \log \frac{(a+b)^2(a^2 - ax + x^2)}{(a+x)^2(a^2 - ab + b^2)}\right)$$

* The subscript on the K is retained to show its identity with that in Eq. (3).

It may be seen that this is a relation between the time (t) and the cube root of the weight at that time or $w^{\frac{1}{3}}$ which has for sim-

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* Owing to that property of similar geometrical solids.

plicity been written as (x). All other values are constants or are known values of (w).

(b) Special Case No. 1. $w_s = w_0$ or $g = a = O$.

In this case the initial weight taken is that equal to the amount necessary for saturation. However, the direct substitution of a $= O$ in Eq. (4) leads to indeterminate results so that a different procedure is adopted. Substituting in Eq. (3), the following is obtained.

Eq. (5). $V(dw/dt) = -K_1 w^{5/3}$ which integrates to give

Eq. (6). $K_2 t = V(w^{-\frac{2}{3}} - w_o^{-\frac{2}{3}})$.

In this, $K_2 = \frac{2}{3}K_1$ or writing with the same letters as in Eq. (4) to show its relation to the general case

$$K_2 t = V(x^{-2} - b^{-2}).$$

(c) Special Case No. 2. The concentration change is negligible.

In this case the concentration is considered as a constant and therefore $(C_s - c)$ is also a constant and the rate is proportional to the surface alone so that Eq. (1) becomes

Eq. (7). $dw/dt = -K_3 w^{\frac{2}{3}}$

The K_3 is different from the other constants and also contains the volume. After completion of the integration we have

Eq. (8) $K_4 t = w_o^{\frac{1}{3}} - w^{\frac{1}{3}}$

where $K_4 = \frac{1}{3} K_3$ or rewriting with the previously used letters

$$K_4 t = b - x.$$

(d) Special Case No. 3. Surface constant.

This is where $S = a$ const. As such it merely becomes submerged in the constant for the entire reaction so that the Noyes-Whitney Law results. From Eq. (1), since $dw/dt = -Vdc/dt$ we obtain the expression $V(dc/dt) = KS(C_s - c)$, or on integration with $t = O$ and $c = O$,

Eq. (9). $At = \ln C_s - \ln(C_s - c)$

where $AV = KS$. When expressed in the "w" notation it becomes $V(dw/dt) = KS(g - w)$, or as $g = w_s - w_o$ and $t = O$ when $w = w_o$, we obtain the Noyes-Whitney Law in the weight-loss notation as,

Eq. (10). $At = \ln w_s - \ln(w_s - w_o + w)$.

If, however, when $t = O$ and $w = w_o$, $c = c_1 = w_1/V$, or the solution already contains some dissolved solid (w_1) at the start, then we have from Eq. (1)

Eq. (11). $At = \ln n - \ln(n - w_o + w)$.

where A is the same as in Eq. (10) and $n = w_s - w_1$, or the amount needed to saturate when $t = O$.

4. Assumptions Involved.

(a) That the process of dissolution takes place normal to the surface and that the effect of the agitation of the liquid against all parts of the surface is essentially the same.

(b) That the crystal shape is predominantly spheroidal throughout its solution and hence its severance into two or more portions is excluded.

(c) That it is not necessary to postulate any definite geometrical shape for the particle undergoing dissolution and therefore no other measurements beyond those of weight are needed.

(d) That under these conditions, the difference in the rates of dissolution from different faces is negligible since all are participating in the combined process to give an average or mean rate.

(e) That the agitation in the neighborhood of the particle is sufficiently intense so that there is no sensible stagnation of the liquid in that region resulting in a slow rate of diffusion being set up. In other words, this law does not apply where there is no agitation.

No assumptions are made concerning the mechanism whereby the solid leaves the surface, such as the postulation of a layer of saturated solution or anything of that nature.

In connection with assumption (c), a considerably more complicated but somewhat similar mathematical formula has been worked out by Murphee (l.c.) on the basis of the use of a characteristic linear dimension of the crystals used. However, in the only experiment given, the solution of dichromate crystals, the form of the crystals was taken as spherical, an assumption which he considered would not introduce any serious error. As the sphere is the geometrical solid with the minimum specific surface,

and as has been seen, the shape of the solid is an extremely important factor, this assumption introduces an artificiality into the entire experiment that renders the results of doubtful value. Theoretically, the basic postulates involved are the same as those used in the derivation of Eq. (4), but the method used in their development is considerably more cumbersome and the results are certainly much more difficult to apply.

5. Discussion.

A careful study of the development of the law will reveal the fact that it contains fundamental elements which permit the extension of its meaning and application to other systems. While the experimental extension into other systems and types of heterogeneous reactions has not been carried very far there is a considerable amount of evidence that it can, very likely be generally applied throughout a wide variety of physical and chemical processes. It would seem to be particularly applicable in those cases where the concentration changes are negligible so that surface change and agitation are the ruling factors in the speed of transformation. It also furnishes a valuable means of studying the kinetics of such changes in a manner that hitherto has not been available. This stressing of the possibility of general application of this law to other systems is particularly important just now in view of the present trend in the study of the kinetics of heterogeneous reactions and the dynamical states of systems which are not in equilibrium.

The quantitative verification of the law, of course, depends on how closely and for how long a time the similarity of shape persists as the particle dissolves. It will be shown that this similarity, in general, continues until the particle is at least half dissolved and in many cases, until it is 75-85 per cent dissolved. It will also be shown that if shape changes do occur that concurrent changes in the values of the constant follow them in the manner that would be expected.

In the particular system chosen for the experimental verification of the law, the numerical value of the constant K depends on the initial amounts of solid and liquid taken, the volume, the agitation and in fact, on all of those variables which influence

the rate of solution in any way. Therefore, the method used has been to hold all of the other variables constant and study but one at a time and compare the values of the constants obtained as a measure of the effect of that variable. In some of the more extreme cases where the agitation is very slow it is there necessary to compare the times of solution, since in these cases stagnation has developed and the application of the law is not justified. Another property of the law which assists in making the study easier is the fact that it is possible to plot the time against some function of the weight (usually algebraic in nature) so that the constant appears as the slope of a straight line.

Although the law was developed for one particle, its extension to the use of a number of particles acts physically to average up a number of disturbing influences and mathematically to cause no important changes in its form. The reason for this is that the change for the use of (n) particles involves the substitution of $(n)^{\frac{2}{3}}$ times the cube root of the sum of the (n) individual weights for the sum of the cube roots of each of the individual weights taken singly. Or, the substitution of $n^{\frac{2}{3}}(w_1 + w_2 + w_3 + \ldots w_n)^{\frac{1}{3}}$ for the expression, $(w_1^{\frac{1}{3}} + w_2^{\frac{1}{3}} + w_3^{\frac{1}{3}} + \ldots w_n^{\frac{1}{3}})$. This is justified even when the value of (n) is small, provided the variation between the particles is small but when the value of (n) is large the variation may be increased considerably. In all of these cases, $n^{\frac{2}{3}}$ appears as part of the constant.

EXPERIMENTAL.

A. THE STUDY OF SURFACE.

Verification of the Cube Root Law.

1. Direct Method.

In most cases the change in weight of the solid was determined by removing it from the liquid and actually weighing it after each time interval. Much care was taken to maintain standard time intervals for its insertion and withdrawal. The times required for its insertion and withdrawal were kept negligible compared with the solution intervals. It was soon found that by the proper choice of materials, concentration, agitation and amount of surface that the rate of solution could be varied over a wide range so that there was no necessity for working with a

rate so fast that sensible errors would be introduced due to the insertion and removal of the solid. When the solid was slightly volatile (as in the case of naphthalene) it was always weighed and handled in tightly stoppered weighing bottles.

2. Indirect Method.

When the distribution of the dissolved solid was sufficiently uniform so that it was apparent that the loss in weight could be computed from the concentration change, the method of withdrawing and analysing samples of the solution was employed. For the lower intensities of agitation this method is unsuitable but it is sufficiently accurate for the higher intensities. For the verification of the law only the direct method was employed.

As both of these methods have long been used in studies of the rates of dissolution, their employment seemed to be justified. The direct method is obviously to be preferred whenever its use is possible since the rate of distribution does not need to be considered. In all cases, unless otherwise stated, the liquid in contact with the surface of the particle was in motion. Complete stagnation was not desired as this would be the condition for diffusion. Also, unless differently stated, the temperature used was $20 \pm 0.2°$ C.

3. The General Law. Eq. (4).

Conditions—Naphthalene, Alcohol (95%), Uniform Free Rotational Agitation.

Method and Apparatus. Container was a cylindrical weighing bottle, 4.1 cm. in diameter and 5.1 cm. high with a capacity of 50 cc., stirred with a small L-shaped single paddle glass agitator at 150 r.p.m. The particle was a common ellipsoidally-shaped naphthalene mothball such as can be purchased at any drugstore. It had evidently been moulded by tightly pressing the ground particles together while they were slightly warm. There were no airholes or irregularities in it at the start nor did any appear during the run. It was well rinsed off with alcohol before using in order to remove surface grains, etc. Its maximum length (L) was 21.5 mm. and its width (W) was 17.5 mm. Ratio L:W =1.23. Weight (W_o) = 3.5324 g. Area = 520 mm². (approx.). Amount of Alcohol used, 28.25 g. (35 cc. at 20° C.) which required a

weight (w_s) of 1.8520 g. of naphthalene for saturation.*

The vessel was kept covered during the run except at the times of insertion and withdrawal of the particle. Constant temperature was maintained by placing the vessel in a large capacity water bath whose temperature did not vary appreciably. As the agitation was not intense enough to move the naphthalene ball it was turned every two minutes by means of a very fine wire. In order for it to receive the same agitation during each period it was always dropped in at the same spot. It was inserted and removed while stirring. After removal it was rapidly dried between filter papers, gently blown with air for a moment and then placed in a weighing bottle and weighed. These operations were all standardized so that they were uniformly executed.

TABLE 1. EXPT. 111.

The General Law.

Time	Δt	Weight	$w^{1/3}$	Eq.(8) $\frac{1}{3}$ Kc_5	Eq.(6) $-\frac{2}{3}$ Kc_5	Eq.(10) log. Kc_5	Eq.(4) $\tan^{-1}$ Kc_5
Min.	Min.	g.					
0	0	3.5324	1.5229	———	———	———	———
5	5	3.4336	1.5086	.0143*	.0082*	.0238*	.01942*
10	5	3.3254	1.4926	.0151	.0088	.0257	.02124
20	10	3.1481	1.4656	.0143	.0086	.0252	.02125
30	10	2.9920	1.4410	.0136	.0084	.0249	.02139
45	15	2.8060	1.4104	.0125	.0079	.0240	.02110
65	20	2.6177	1.3782	.0111	.0073	.0227	.02051
				———	———	———	———
		Mean (*omitted)=		.0133	.0082	.0245	.02110
		Average Deviation from Mean or Ave. D/M =		9.1%	5.7%	3.7%	1.1%

Note—This Kc_5 is equal to the $(Ka^2)/V$ in the equation, for the significance of the (c) as a superscript see the next experiment. The amount of naphthalene dissolved was 0.9147 g. or about 26% of its initial weight. The equation numbers (4, 6, 8, 10) refer to those of the corresponding equations in the theoretical part.

* The solubility of naphthalene in 95% alcohol was determined experimentally. The following data were obtained by use of the freezing point method. At 11.9° C., 20.1750 g. of alcohol dissolve 1.0 g.; at 14.8° C., 1.1 g. and at 22.1° C., 1.4 g. of naphthalene. A curve plotted from these values gave a solubility of 6.56 g. of naphthalene per 100 g. of 95% alcohol at 20° C. This region of the curve was also checked with a larger amount of alcohol and found to be correct.

The concentration of the dissolved naphthalene rose from a zero per cent saturated solution to a forty-nine per cent saturated solution.*

At the end the naphthalene ball showed a slight change of shape, it then having a length of 19 mm. and a width of 16 mm. Ratio L:W = 1.19. When compared with the ratio of 1.23 at the start, it shows a slight rounding which is reflected in the decreased value of the constant, due to a decrease in the specific surface. Sharpening, on the other hand, involves an increase of the specific surface and therefore increases the value of the constant. While the naphthalene balls used in this work could not be called strictly homogeneous in structure, they were always found to be without air bubbles, holes or cracks of any kind, no matter how thin a section was prepared. It was not possible to correlate any irregularity of action with their structural composition. The particles of which they were composed were crystalline in character. (see p. 74).

In the columns of constants which are calculated according to the equations designated, there is a comparison of the closeness with which each of the equations fit the experimental data. The first value in each case has been omitted from the mean on account of the common uncertainty regarding the first determination, due to possible initial surface irregularities which sometimes cannot be eliminated. If we assume that the magnitude of the average deviation from the mean is a measure of the relative closeness with which a given formula fits the observed values, the interesting effect of introducing the concentration into the formulae is easily noticeable. Eq. (8), where the concentration is considered as constant, is, of course, out of the question. The data show clearly that the application of Eq. (4) is justified although the logarithmic formula is also close. However, since the latter is based on the assumption of constant surface, this closeness must be incidental as the next section will show.

No further attempt will be made to describe the agitation,

* This manner of describing the concentration will be found most suitable for comparative purposes in this kind of work. Washburn, Principles of Physical Chemistry, 1st Ed. (1915) p. 277.

first, on account of the difficulty of specifying it and second, because it is felt that its uniformity is more important than its type. As it will be seen later, the wide variety of types through which the law holds confirms this conclusion.

Finally, the laborious calculations involved in the use of Eq. (4) acted as a deterrent in its general use in the study of other variables so that the more easily calculated special cases were chosen for the remainder of the work.

4. Special Case No. 1. Eq. (6). $W_o = W_s$.

Conditions—Naphthalene, Alcohol (95%), Uniform Free Rotational Agitation.

Method and Apparatus. 250 cc. Pyrex beaker. Small glass agitator running at 518 r.p.m. Naphthalene ball similar to that used in the last experiment. Length 21.5 mm. Width 17.5 mm. Ratio L:W = 1.23. There was no motion of the ball due to the agitation but it was periodically turned with a wire as in Expt. 111 and the same general precautions were observed. Insertion and removal without stopping the stirrer. Weight of the naphthalene ball = $w_o = w_s = 3.8752$ g. Weight of alcohol taken was 59.00 g. as this is the amount of alcohol just saturated by this weight of naphthalene at 20° C.

TABLE 2. EXPT. 112A.

Special Case No. 1.

Time	Δt	Weight	$w^{-2/3}$	Kp_{10} Eq.(8)	Kp_{10} Eq.(10)	Kp_{10} Eq.(6)
Min.	Min.	g.		1/3	N.W.L.	-2/3
0	0	3.8752	.4053	------	------	------
10	10	3.6041	.4254	.0375	.00210	.0201
30	20	3.1477	.4656	.0338	.00196	.0201
50	20	2.7691	.5071	.0306	.00185	.0207
70*	20	2.4628	.5483	.0269	.00169	.0206
110	40	2.0058	.6287	.0223	.00148	.0201
			Mean =	.0302	.00181	.0203
			Ave. D/M =	26%	10.3%	1.2%

Note—The values of the constants in this table are obtained by progressively calculating from one period to the other e. g. $Kp_{10} = .5\,(w^{-2/3}_{30} - w^{-2/3}_{10})$, etc., and will be called the "progressive constants"

(K_P),† in contrast to the "cumulative constants" (K^c), which are obtained by calculating each period independently from zero time and which were used in the last experiment, e. g. $K^c_{10} = 1/7\ (w^{-\frac{2}{3}}_{70} - w^{-\frac{2}{3}}_{0})$.* The ball was measured at this point giving a length of 18 mm. and width of 14.5 mm. Ratio L : W = 1.24. Its shape was practically that at the start. It had lost 36.5% of its weight. At the end of the final time interval it had lost 48.5% of its initial weight and the solution concentration was similarly 48.5% saturated. At the end the ball was quite smooth and showed no etching or corrosion except for one barely noticeable pit about 1 mm. in diameter and 0.5 mm. deep. Any change in shape from the original was so slight that it was inappreciable.

In order to show the effect of a change in shape, the agitator in Expt. 112A was replaced by a larger one running at 290 r.p.m. This produced a more intensive agitation and caused the ball to roll around continually. In this case it was necessary to stop the agitator each time in order to remove the ball but the time required for this operation was only two or three seconds and was negligible in comparison with the total length of the time interval. With these exceptions, everything else was the same as in the first part of the experiment.

TABLE 3. EXPT. 112B.

Special Case No. 1. Change of Shape.

Time	Δt	Weight	$w^{-\frac{2}{3}}$	K_{10} Eq.(8)	K_{10} Eq.(10)	K_{10} Eq.(6)	
Min.	Min.	g.		⅓	N.W.L.	−⅔	
0	0	2.0058	.6287	——	——	——	Still in good shape.
10	10	1.8479	.6649	.0340	.00237	.0362	Band on side rounding off. No pitting.
30	20	1.6027	.7302	.0284	.00206	.0326	Band practically gone but still smooth.
70	40	1.2639	.8554	.0222	.00172	.0313	Same. Elliptical in cross-section. Not pitted.

Note—Final length was 11 mm. Width was 8 mm. Ratio L : W = 1.37. Solution was now 67.5% saturated and the particle had lost 67.5% of its initial weight since the start in Part A. During Part B the concentration change was almost 20%, i. e. from 48.5% to 67.5%.

† A mean of the K^c values tends to represent the experiment as a whole when compared to others, while the K_P values show better how the action progresses in each case in particular. Hereafter in this dissertation, the K_P values will be used without the superscript unless otherwise designated.

The predominating change of shape was in the direction of rounding, especially on the sides where the band about the mid-part of the ball disappeared completely. This was due to the fact that the ball rolled about its major axis and wobbled considerably. The final body was tending towards a spindle-shaped figure. Due to these effects, the L:W ratio does not indicate what happened in the main change of shape that occurred. This shows that the two types of shape change can occur simultaneously, viz., rounding and sharpening. The constants for the different equations are tabulated and it is interesting to compare the relative percentages of change in their values caused by the change of shape in this part of the experiment. For Eq. (8) the constant for the final period had changed by an amount equal to 34.7% of its value for the first period. Similarly, the constant calculated by the Noyes-Whitney Law of Eq. (10) had changed 27.4%, while that calculated by Eq. (6) had changed but 13.5%.

In the first part of the experiment where the shape change was practically negligible, the deviation of the constant calculated by Eq. (6) is highly satisfactory especially when the range of concentration of almost 50% is considered. The definite failure of the Noyes-Whitney Law to give a satisfactory constant under conditions of surface change was also to be expected and confirms the statement made in the last section on p. 40.

Comparing the rate in the first part with the initial rate in the second part, the increased agitation in the second part is shown to have almost doubled the velocity of dissolution. This quick response to changes in agitation indicates the importance of keeping the agitation uniform during the run.

5. Special Case No. 2. Eq. (8). No Concentration Change.

As this form of the general law is the most easily applied and calculated, it was soon found that its use was much more convenient and expeditious than the other possible forms. Due to this fact, its verification under many varied conditions was easily possible. Several of the experiments will be here presented while others may be found in different sections where the main object was the study of some particular variable and not the law itself.

Conditions—Naphthalene, Benzene, Uniform Free Rotational Agitation.

Method and Apparatus. Cylindrical crystallizing dish, 7.6 cm. in diameter and 4.5 cm. deep. Glass L-shaped agitator with blade about .75 cm^2. in area and running at 83 r.p.m. Naphthalene ball as before weighing 3.7443 g. 110 cc. of benzene solution containing 2.04 g. of dissolved naphthalene. Weight of naphthalene needed to saturate $= w_s = 61.0$ g. Temperature 23° C. Insertion and removal during stirring. The agitation was not intense enough to move the ball around but did cause it to shift its position slightly from time to time. The dish was placed in a water bath of large heat capacity so that the temperature was constant within a tenth of a degree throughout the experiment.

TABLE 4. EXPT. 109.

Special Case No. 2. Naphthalene—Benzene.

Time Min.	Δt Min.	Weight g.	$w^{1/3}$	$K_{.5}$ Eq.(8)	
0.0	0.0	3.7443	1.5528	------	
0.5	.5	3.5012	1.5184	.0344	Surface in good condition.
1.0	.5	3.3038	1.4893	.0291	Surface in good condition.
1.5	.5	3.0937	1.4571	.0322	Very slightly pitted, all very small.
2.0	.5	2.8951	1.4251	.0319	Several pits slightly deeper.
2.5	.5	2.7065	1.3936	.0326	Slightly more pitted. Some .5 mm. deep.
3.5	1.0	2.3682	1.3329	.0304	Still more corrosion and shape altering.
4.5	1.0	2.0312	1.2664	.0333	Indented badly. One end much pitted
				———	and shape changing fast, especially
(a)			Mean =	.0319	one end.
		Ave. D/M = 4.0%			
5.5	1.0	1.7062	1.1949	.0358	Pitted and shape considerably worse.
6.5	1.0	1.4026	1.1193	.0378	Estimate two-thirds of surface not pitted, but remainder very bad with the shape changed markedly.

Note—Initial concentration, 3.3% Satd.; at point (a) 4.5% Satd.; final 7.2% Satd. Weight loss up to (a) was 45%, total weight loss 63%.

The rapidity of solution required the employment of short time intervals in order to prevent much shape deformation, which, nevertheless, became considerable with the one minute periods in the latter parts of the experiment. In the case of very soluble solids, the difficulty of pitting and surface-increase is al-

ways encountered, especially if the saturation concentration is low. The effect of this is easily seen in the constant after the point (a) was reached. The extent of pitting tends to increase rather than to decrease as the dissolution proceeds. This is particularly true if the condition of flow of the solvent around the solid tends to stagnancy and the solid is relatively quite soluble in the liquid. This is very probably the reason why the previous work on solution has been carried on with either slightly soluble solids or if the more soluble solids were used, to employ highly concentrated solutions. This property must not be confused with the production of the so-called etch figures which are due to the anisotropic solubilities of the solid itself.

An example of a system whose components are inorganic compounds will next be given.

Conditions—Very irregular crystalline particle of Blue Vitriol, Water, Uniform Free Rotational Agitation.

Method and Apparatus. 100 cc. Pyrex beaker. Same agitator as Expt. 109 but running at 152 r.p.m. Particle did not move. It was rinsed and dried before use and possessed no visible checks, cracks or irregularities of composition. Always placed in the same spot in the beaker for each interval. Inserted and removed during stirring. 70 cc. of water at 25° C. Weight of $CuSO_4$, 5 H_2O needed to saturate, 15.9 g.

TABLE 5. EXPT. 108B.

Special Case No. 2. Blue Vitriol—Water.

Time Min.	Δt Min.	Weight g.	$w^{1/3}$	K_1 Eq.(8)
0	0	6.9229	1.9059	———
1	1	6.5540	1.8714	.0345
2	1	6.2171	1.8388	.0326
3	1	5.8893	1.8058	.0330
4	1	5.5772	1.7734	.0324
5	1	5.2607	1.7392	.0342

Mean = .0333
Ave. D/M = 2.4%

Note—During the first three intervals, the same side of the particle lay upward. It lost a total of 24% of its initial weight and the concen-

tration rose from zero to 10.4% Satd. At the end the particle appeared to have its initial shape except that one tip was sharply serrated, this having occurred largely during the final interval.

Experiment giving a further illustration of a system using inorganic components.

Conditions—Irregular, natural salt particles (NaCl), Water, Uniform Free Rotational Agitation.

Method and Apparatus. 4.1 Pyrex beaker, 15.5 cm. in diameter. 2.0 kilos of water at 20° C. Standard straight iron paddle agitator, 4.25″ long by 1″ wide set at .5″ up from the bottom at the center and running at 241 r.p.m. Indirect method of analysis, i. e., samples of approximately 20 cc. of solution were taken from the top by dipping at a point halfway from the center to the wall of the beaker. The weight remaining undissolved was calculated from the percentage of solids obtained on evaporation of weighed amounts of these samples. The salt used was a carefully sieved (twice by hand) 3-4 Tyler Standard Sieve cut* of a natural mined rock salt. Weight taken, 40.0 g. On the average this amount would contain 177 particles of an average weight of .2230 g. Of this weight there was .479 g. of insoluble material for which a correction was made. The salt was not otherwise treated before use.

TABLE 6. EXPT. 53.

Special Case No. 2. Rock Salt—Water.

Time	Δt	Conc. G./100	Weight Diss'd.	%	Weight	$w^{1/3}$	K_{15}
Sec.	Sec.	g. H_2O	(20 x Conc.)	Diss'd.	g.		Eq.(8)
0	0	.000	0.00	0.0	39.521	3.4062	———
15	15	.390	7.80	19.7	31.721	3.1655	.2407
30	15	.758	15.16	38.4	24.361	2.8989	.2666
45	15	1.048	20.96	53.0	18.561	2.6477	.2512
60	15	1.294	25.88	65.5	13.643	2.3895	.2582
77	17	1.537	30.74	77.7	8.783	2.0632	.2880
90	13	1.676	33.53	85.0	5.993	1.8168	.2840
105	15	1.802	36.05	91.2	3.475	1.5146	.3022

* This designation of screen size is used for brevity. It indicates that the material passed through the No. 3 mesh and was retained on the No. 4 mesh screen of this series.

TABLE 6—(continued)

Time	Δt	Conc. G./100 g. H_2O	Weight Diss'd. (20 x Conc.)	% Diss'd.	Weight g.	$w^{1/3}$	K_{15} Eq.(8)
Sec.	Sec.						
120	15	1.894	37.89	96.0	1.629	1.1766	.3380
135	15	1.955	39.11	99.0	.411	.7435	.4331

From 0 to 85% Diss'd. Mean (0 to 90 sec.) = .2647
Ave. D/M = 5.5%
From 0 to 65% Diss'd. Mean (0 to 60 sec.) = .2541
Ave. D/M = 3.3%

Note—The values for 15, 120 and 135 seconds are in doubt, the first due to uncertainty about the exact zero time of the establishment of the regime which was to predominate through the larger part of the dissolution and the others because of the small differences in the analyses.

The agitation here was very vigorous with a vortex of approximately 3.75″ being obtained. The particles moved about very rapidly, circling around at a distance of one or two inches from the center. After about 75 sec. they became so small that they began to travel near the outer edge of the beaker and at 105 sec. a considerable number of them were above the agitator blade. This probably accounts for the faster rate and the higher value of the constant observed for this time. Such irregularities may be expected in the case of very high intensities of agitation and especially with the use of the indirect method of analysis. For this reason the later values should not be taken too seriously. However, it is seen that up to the point where more than 60% of the solid is dissolved, the constant holds quite satisfactorily. It can also be added that this experiment is quite a severe test of the application of the law due to its freedom from the imposition of "artificial" conditions since it represented the actual, ordinary operation of dissolving a solid in the common laboratory and plant manner.

Only a lack of space prevents the presentation of many other experiments in which this form of the law was tested and found to hold to the same extent as it does in those which have been given. Many of these will be described in connection with the study of other variables. In all cases, though, the range in the percentage of the material dissolved should be taken into consid-

eration in connection with the range over which the mean value of the constant may be computed. With the concentration change negligible and the agitation uniform, one may reasonably expect that the velocity constant over a range of half of the material dissolved will have substantially the same value. On the other hand, with the above factors uniformly controlled, it has invariably been found that a variation of the constant was accompanied by a change in the shape characteristics of the particles.

6. Special Case No. 3. Eq. (10, 11). The Noyes-Whitney Law. Constant Surface.

Since the previous work on this law has been done in a different manner and under different conditions from those to be presented here, this portion is mainly interesting as an additional confirmatory proof of this special case of the more general law of Eq. (4). ([33, 34, 41]).

Conditions—Naphthalene balls, Alcohol (95%), Uniform Free Rotational Agitation.

Method and Apparatus. A number of naphthalene balls were prepared and weighed and eight of them were selected whose weights were very close to each other. Each one was allowed to dissolve for a short period of time in a solution of naphthalene in alcohol. Six different solutions were prepared for this purpose, each having a different concentration. Each of the solutions was made up from 80.2 g. of 95% alcohol in which the calculated amount of naphthalene had been dissolved. The solutions chosen had the following concentrations in terms of per cent saturation: 0, 8.61, 21.53, 43.05, 64.59, 85.0. Each solution was treated with one naphthalene ball for one period only and since they were all of the same shape and size (by selection), the combined results formed a series in which the surface change may be regarded as constant. In this series the concentration was the only variable. The weight (w_s) of naphthalene necessary for saturation of the weight of alcohol taken was 5.2611 g. Mean weight of the balls was 3.9810 g. Ave. D/M = .5%. Max. D/M = 1.1% (A″, a check run). 250 cc. Pyrex beaker with a glass agitator at 292 r.p.m. The balls rolled around the outer wall throughout the entire per-

iod. They were inserted during the stirring but removed with the agitator stopped, the process of removal requiring about 2-3 seconds for its accomplishment. The temperature was maintained at 20° C. by placing the beaker in a water bath of three gallons capacity which was stirred from time to time.

TABLE 7. EXPT. 115.

Special Case No. 3. N. W. L. Naphthalene—Alcohol.

No.	Conc. % Satd.	a g.	n = w_s–a	w_o g.	Δt Min.	w g.	$\frac{w_o}{w}$	$\frac{n}{(w_o-w)}$	K_5 Eq. 11
A′	0.00	.0000	5.2611	3.9868	5	3.7130	.2738	4.9873	.0242
A″	0.00	.0000	5.2611	3.9343	5	3.6108	.3235	4.9376	.0275
B	8.61	.4531	4.8080	4.0130	5	3.7301	.2829	4.5251	.0263
C	21.53	1.1328	4.1283	3.9617	7	3.6242	.3375	3.7908	.0264
D	43.05	2.2654	2.9957	3.9913	10	3.6799	.3114	2.6843	.0238
E	64.59	3.3984	1.8627	4.0024	15	3.7126	.2898	1.5729	.0245
E″	64.59	3.3984	1.8627	3.9869	5	3.8762	.1107	1.7520	.0266
F	85.00	4.4719	.7892	3.9716	15	3.8595	.1121	.6771	.0222

TABLE 8.

Tabulation of the Constants in Table 7.

No.	Conc. % Satd.	K_5* Eq. 11
A	0.00	.0258
B	8.61	.0263
C	21.53	.0264
D	43.05	.0238
E	64.59	.0256
F	85.00	.0222
		Mean = .0250
		Ave. D/M = 5.2%

Note—Weight of naphthalene previously dissolved in each solution = a, and n = w_s — a is the weight of naphthalene needed for each solution in order to completely saturate it. * Average values.

While it is realized that the assumption of constant surface conditions is not rigidly justified, it is felt that the approximate constancy obtained must be considered in connection with the very wide range of conncentrations studied. The experiment as it was carried out also involved a comparison between different

particles which very likely accounts for some of the deviations obtained. ([33, 35, 39]). Moreover, it might be well to add that the precision obtained throughout this entire work upon the surface effect compares excellently with that reported by other investigators who have worked in this field.

7. Special Case No. 4. Shape Constant, Surface Varying. Rate per Unit Area.

In addition to the above experiments, it also seemed desirable to show still more clearly the dependence of the rate of solution upon the surface, so the following experiment embodying the above mentioned factors was made.

Conditions — Naphthalene, Alcohol (95%), Impeded Rotational Agitation.

Method and Apparatus. Two cylindrical pieces of naphthalene whose cross sections were circles of different sizes were fashioned from two of the balls such as previously described. After carefully polishing the flat circular end of each one, it was rinsed off with alcohol, dried and weighed. The method consisted in presenting this flat end to the dissolving action of the solvent for a given time interval after which it was weighed to determine the loss in weight. In order to prevent action of the alcohol upon any portion of the particle than that desired, the following procedure was adopted. The particle was inserted into the end of a squarely-cut piece of pure gum tubing so that it was firmly and tightly grasped by the tube. The flat circular end of the particle protruded about 1 mm. below the edge of the tubing. The other end of the tubing was fitted over the end of a glass rod so that it could be lowered into the alcohol to exactly the same position for each time interval.

When it was in position the flat circular end of the exposed solid was horizontal with its face downward and the tight rubber tube grasping it prevented any solvent action on the particle above the uncovered portion. Container was a 600 cc. beaker (Pyrex) stirred with a standard straight iron paddle agitator 2″ long and 1″ wide running at 82 r.p.m. This was classified as impeded rotational agitation because the naphthalene and the rod

acted as an impeding barrier to the motion of the liquid. The alcohol used weighed 307 g. and contained 2.492 g. of dissolved naphthalene (10.6% Satd.). The temperature was held constant in the usual manner at 22.5° C. The surface of the solid was placed at a distance of 1.25 cm. below the surface of the liquid with its outer edge 1.1 cm. from the wall of the beaker. It was inserted and removed without stopping the stirring.

Piece "A" was 14.25 mm. in diameter with an area of 1.60 cm^2.

Piece "B" was 17.50 mm. in diameter with an area of 2.40 cm .

TABLE 9. EXPT. 117.

Special Case No. 4. Shape Constant.

Δt	Weight w	Δw	Δw per	Δw/cm^2/Min.
Min.	g.	g.	Min.	
Piece "A" — 1.60 $cm.^2$				
0	2.3620	———	———	———
5	2.3125	.0495*	———	———
5	2.2644	.0481	.00962	.00601
10	2.1671	.0973	.00973	.00608
6	2.1086	.0585	.00975	.00609
			———	———
		Averages =	.00970	.00606
		Ave. D/M =	0.5%	0.5%
Piece "B" — 2.40 $cm.^2$				
0	3.0433	———	———	———
5	2.9715	.0718	.01436	.00598
5	2.9008	.0707	.01414	.00589
0*	2.7273	———	———	———
7	2.6621	.0990	.01414	.00589
			———	———
		Averages =	.01421	.00592
		Ave. D/M =	0.7%	0.7%

Note—*Rejected due to surface hollowing out thus causing a change of shape. The total change of concentration for both was less than 2.5% Satd.

The quite satisfactory agreement for the two different areas shows that, other things equal, the rate of solution is strictly proportional to the first power of the surface. Thus, with the agitation uniform and the shape constant, the velocity will vary di-

rectly as the surface changes and this is the fact upon which the derivation of the general law has been based.

8. Conclusions.

The experimental data set forth in the preceding tables and the interpretative comment which follows each one have had for their purpose the verification and confirmation of the Cube Root Law from both the general and specific points of view. It is believed that these purposes have been satisfactorily accomplished.

OTHER TYPES OF AGITATION.

The intent of this section is to show that the operation of the law is not limited to any particular type of agitation, provided that it is uniformly periodic in its nature. Due to its simplicity and convenience, the law in the form of the special case No. 2., Eq. (8) of no concentration change, will be used.

1. Impeded Rotational Type.

The experiment last described has been considered as belonging to this type. Another way in which this type of agitation may be obtained results when the solid is held in a screen or basket-like container which may be suspended or immersed in the liquid. In this case the flow of the fluid is impeded as it passes through the stationary mass. Another way in which impeded agitation may be produced is to place baffles in the container but still allow the solid to move freely. The latter case will not be considered here but will be described later under the larger scale experiments. Several experiments which will illustrate the operation of the law in this type of agitation will follow.

Expt. 125.

Conditions—Irregular Salt Particles, Water, Impeded Rotational Agitation.

Method and Apparatus. 4.1. Pyrex beaker. Standard straight iron paddle agitator, 3.75″ long and 1″ wide, set at center and .5″ off the bottom, running at 82 r.p.m. 4.0 kilos of water at 20° C. 40.00 g. of irregular salt particles, a 2-3 mesh Tyler standard screen cut with an approximate average weight of .5 g. They

were held in a hemispherical screen (2″ in diameter) of about 15 mesh and lowered into the water at the top at exactly the same spot for each time interval. Inserted and removed during stirring. On removal, the screen and its contents were instantly submerged in alcohol after which they were washed, decanted, dried and weighed.

TABLE 10. EXPT. 125.

Impeded Rotational Agitation (1).

Time Min.	Δt Min.	Weight g.	% Diss'd.	$w^{⅓}$	K_1 Eq.(8)	
0	0	40.0000	0.0	3.4199	———	Several particles above water.
1	1	31.0795	22.2	3.1440	.2759	All now under water.
2	1	22.9673	42.5	2.8425	.3015	
3	1	16.2972	59.5	2.5353	.3072	
4	1	11.0569	72.3	2.2278	.3075	
5	1	6.9613	82.5	1.9094	.3184	Many now with sharp edges.

Mean = .3021
Ave. D/M = 3.5%

Expt. 126.

Conditions—Same as in Expt. 125.

Method and Apparatus. Same as in Expt. 125 but used 20.00 g. of a different sample of salt, a 2-3 mesh screen cut containing 43 particles. Average weight, .465 g. Temperature 21.5° C.

TABLE 11. EXPT. 126.

Impeded Rotational Agitation (2).

Time Min.	Δt Min.	Weight g.	% Diss'd.	$w^{⅓}$	$K_{.5}$ Eq. (8)
.00	.00	20.0000	0.0	2.7144	——— (1)
.55	.55	16.7147	16.5	2.5568	.1432
1.05	.50	13.9945	30.0	2.4092	.1476
1.55	.50	11.6534	42.0	2.2671	.1421
2.05	.50	9.4140	53.0	2.1115	.1556 (2)
2.55	.50	7.4560	62.5	1.9534	.1581 (3)

Mean = .1493
Ave. D/M = 4.0%

Note—(1) Conditions satisfactory. (2) 44 crystals now, i. e. one appeared between 1.55 and 2.05. Many sharp edges showing. (3) Same number but many more sharp points.

Expt. 127B.

Conditions—Irregular salt particles. 90% Satd. salt solution.

Method and Apparatus. 1,000 cc. casserole. Standard straight iron paddle agitator 3″ long and 1″ wide running at 82 r.p.m. Same screen as in Expt. 126. Other things equal with the exception of 5.00 g. of an 8-10 mesh screen cut of salt particles containing 366 particles of an average weight of .0137 g. Temperature 20° C.

TABLE 12. EXPT. 127B.
Impeded Rotational Agitation (3).
Ninety Per Cent Saturated Salt Solution.

Time Min.	Δt Min.	Weight g.	% Diss'd.	w′%	K_1 Eq. (8)
0	0	5.0000	0	1.7099	——
1	1	4.4013	12	1.6388	.0711
2	1	3.9054	22	1.5747	.0641
3	1	3.4470	32	1.5106	.0641
4	1	3.0425	40	1.4490	.0616
5	1	2.6521	47	1.3842	.0648
6	1	2.2574	55	1.3118	.0724 (1)
7	1	1.8976	62	1.2380	.0738 (2)
8.05	1.05	1.5605	—	1.1599	.0743 (3)
9.05	1	1.2329	—	1.0722	.0877 (4)

Mean (0 to 5 Min.) = .0651

Note—(1) Some particles very small. (2) Some fell through the screen. (3) Same as (2). (4) 331 particles left—loss of 35. The last four periods are in doubt due to the fact that the particles had become so small that they kept sifting through the screen from time to time. If it is assumed that the entire 35 were lost in the last three periods and the weights are corrected back on the basis of those lost having the same average weight as those left, constants of .062 and .060 are obtained.

2. **Straight-Line Flow or Uni-Directional Type.**

This term is not to be taken in the sense of viscous flow but merely denotes that the main body of the liquid and solution moves in one direction only.

Conditions—Irregular Salt Particles. Water.

Method and Apparatus. A glass tube 28 cm. long and 11 mm. inside diameter was fastened at a ten degree angle from the horizontal. The lower end was connected with a large bottle of water by means of a rubber tube which acted as a siphoning arrange-

ment so that a head of about two feet was obtained. The rubber tube was large enough so that a flow of about 400 cc. (.5″ of head) of water was obtained for a time interval of 15 sec. A spring pinchcock was placed in the line just before the glass tube. The salt particles were inserted into the upper end of the tube and over the end of the latter a screen of about four mesh was arranged in such a manner that its removal was easily and rapidly accomplished. Behind the particles there was a small wire which had been bent into the form of a rake and having its handle outside the end of the tube. This was used for the purpose of pulling out the particles at the end of the period.

Before the beginning of the period, the water level was allowed to rise to about a centimeter behind the particles, so that on the opening of the pinchcock the tube would at once fill completely with water. This permitted no air bubbles in the tube and prevented any of the solution from flowing downwards towards the lower end. After the end of the alloted time (15 sec.) the pinchcock was closed, the screen removed and the particles raked out into a beaker of alcohol. They were then washed, dried and weighed. The same head was maintained for each period by the addition of an equal volume of water to the reservoir. With practice, it became possible to standardize this operation so that about three seconds were required to get the particles into the alcohol after the closing of the pinchcock at the end of the flow period. The entire experiment was run at the temperature of the room or 25° C. The salt particles used were of the usual irregular shape and nature and consisted of 10 particles of a 2-3 mesh screen cut and weighed 4.9190 g.

TABLE 13. EXPT. 132B.

Straight-Line Flow.

Time Sec.	Δt Sec.	cc. of Flow	Weight g.	% Diss'd.	$w^{1/4}$	K_{15} Eq. (8)
0	0	0	4.9190	0.0	1.7007	-----
30	30	760	2.5381	28.0	1.3641	.1683
45	15	385	1.5952	67.5	1.1684	.1957
60	15	395	.9174	81.3	.9717	.1967
75	15	400	.4793	90.4	.7826	.1891

Mean = .1874

Ave. D/M = 5.1%

Note—The blocking effect of the larger amount of particles for the first period can be seen both in the decreased volume of flow and also in the value of the constant.

A rapid rate of flow was necessary in order to prevent any motion of the solution in a countercurrent direction. Even then, the resulting rate of solution was so fast that greater variations in the value of the constant could have been expected than those that were obtained. In this particular case, the volume of the salt particles at the start was large compared to the cross section of the flow, a factor that was mentioned on p. 26.

3. Straight-Line Flow—Partly Countercurrent.

Conditions—Irregular Salt Particles. Water.

Method and Apparatus. The long tube of the previous experiment (132B) was replaced by a glass Gooch crucible holder, 1.25″ in diameter and 3″ long which was held upright with the constricted part below connected to the rubber tubing and water reservoir as before. Inside the holder, a small basket-like grid of wire was suspended from the top so that it would support a salt particle at a point about one inch below the top or below the surface when the holder was full of running water. The grid was easily and rapidly removable so that it could be immersed in alcohol in order to stop the dissolving action of the adhering water. The operation consisted in simultaneously dropping in the particle and opening the pinchcock, allowing the water to flow vertically upward for 30 sec., then stopping the flow and instantly removing the grid and particle to the alcohol. Washed and dried as usual. The head was kept constant and the temperature was 25° C. (room). In spite of the strong upward flow, the particle dissolved with a number of currents of solution moving downward against the main current of the stream, i. e., counter-current. Head of water was 22″ (throttled down slightly).

TABLE 14. EXPT. 132A.

Straight-Line Flow—Partly Countercurrent.

Time 30 sec. Per.	Δt Per.	cc. of Flow	Weight g.	% Diss'd.	$w^{1/3}$	K_1 Eq. (8)
0	0	0	1.1028	0.0	1.0332	———
1	1	84	1.0248	7.1	1.0082	.0250
2	1	85	.9507	13.5	.9833	.0249
3	1	88	.8744	20.5	.9563	.0270
4	1	88	.8014	27.2	.9289	.0274
5	1	86	.7277	34.0	.8995	.0294
6	1	91	.6602	40.0	.8708	.0287
7	1	90	.6060	45.0	.8462	.0246
8	1	88	.5406	50.5	.8146	.0316*
9	1	89	.4896	55.4	.7882	.0264
11	2	178	.3905	64.3	.7309	.0286

Mean (*omitted) = .0268
Ave. D/M = 5.5%

Note—There was very little change in shape of the particle.

4. Tumbler Type.

Expt. 130A.

Conditions—Irregular Salt Particle. Water.

Method and Apparatus. An ordinary 8″ test tube was used as the container. A board was provided with two clamps into which the test tube could be quickly inserted and removed. This board was mounted on an axis so that when the test tube was in the clamps, the uniform rotation of the board (which was geared to a small motor) turned the test tube end over end, so that its contents tumbled from one end to the other as the rotation proceeded. 25 cc. of water at a temperature of 25° C. were pipetted into the test tube for each time interval. This amount occupied about 35% of the available volume in the stoppered tube so that during the rotation considerable turbulence was originated. The rotator was steady and ran at the rate of one turn every eleven seconds. The runs were made at room temperature or 25° C.

The operation which was practised until it was well standardized was as follows. With the water in the test tube which was in

position in the clamps, the particle of salt was dropped in, the stopper inserted and the rotator started.

At exactly four rotations (44 seconds) the rotator was stopped, the tube removed, unstoppered and its contents dumped on a screen from which the parrticle fell into a beaker of alcohol. From here it was washed by decantation in the alcohol and dried and weighed in the usual manner. The operations involving the removal of the particle took about three seconds and this was regarded as part of the time interval. Only one particle was used and it weighed 1.2943 g.

TABLE 15. EXPT. 130A.

Tumbler Type. One Particle (1).

Expt. 130A.

Total Turns	Δt Turns	Weight g.	% Diss'd.	$w^{1/3}$	K_{4t} Eq. (8)
0	0	1.2943	0.0	1.0898	———
9	9	.9017	32.4	.9661	.0550
13	4	.7440	42.5	.9061	.0600
17	4	.6103	52.5	.8482	.0579
21	4	.4924	62.0	.7897	.0585
25	4	.3895	69.5	.7303	.0594
29	4	.3034	76.5	.6719	.0584
					Mean = .0582
					Ave. D/M = 2.2%

Expt. 130B.*

0	0	1.2687	0.0	1.0826	———
4	4	1.0714	15.6	1.0233	.0593
8	4	.9028	29.0	.9665	.0568
12	4	.7539	40.5	.9101	.0564
16	4	.6196	51.5	.8525	.0576
20	4	.4991	60.6	.7932	.0593
24	4	.3952	69.0	.7339	.0593
28	4	.3080	76.0	.6753	.0586
					Mean = .0582
					Ave. D/M = 1.8%

Note—No particular change of shape in either experiment. * Conditions same as in 130A but used one particle whose shape differed but little from that used before.

Expt. 131A.†

0	0	5.0000	0.0	1.7100	-----
4	4	3.2568	35.0	1.4822	.2278
8	4	1.9402	61.5	1.2472	.2350

Mean = .2314
Ave. D/M = 1.5%

Note—† Conditions same as for the above experiments but used 35 cc. of water each time and instead of one particle used 5 g. of a 4-6 mesh Tyler screen cut of salt that contained 62 particles. The mechanical loss of a crystal at the end of the second time interval caused the experiment to be stopped.

Expt. 131B.

Conditions—Same as in Expts. 130A-B, 131A.

Method and Apparatus. Same as in Part A but use 5.g. of a 3-4 mesh Tyler screen cut of the same salt containing 21 particles.

TABLE 16. EXPT. 131B.

Tumbler Type. 21 Particles (2).

Total Turns	Δt Turns	Weight g.	% Diss'd.	$w^{1/3}$	K_{4t} Eq. (8)	
0	0	5.0000	0.0	1.7100	-----	
4	4	3.7439	25.0	1.5527	.1573	
8	4	2.6825	46.4	1.3894	.1633	
12	4	1.8138	63.7	1.2195	.1699	
16	4	1.1498	77.0	1.0476	.1719	(1)
24	8	.4271	91.0	.7531	.1472	(2)*

Mean (*omitted) = .1656
Ave. D/M = 3.2%

Note—(1) Some crystals stuck to the wall on the last two turns. (2) Estimate that three-fourths of the particles stuck to the walls on each turn. Considerable variation in size at the end probably due to the fact that many of the particles did not drop down from the wall of the tube when it turned. This did not happen in the other experiments because the particles did not get small enough to do this. For this reason the last value is omitted from the mean.

These four experiments were given as it was felt that if the law continued to hold under these conditions it had survived a rather severe test due to the more or less random nature of the

type of agitation involved. The results, in spite of the operative difficulties encountered in the last one, are considered quite satisfactory.

5. Ball Mill Type.

Conditions—Irregular Salt Particle. Water.

Method and Apparatus. An ordinary 5 lb., wide-mouthed chemical bottle was fastened to the rotator board used in the preceeding experiments in such a way that it rotated horizontally about its central axis in the manner of a ball mill. 250 cc. of water were placed in the bottle for the entire experiment. This amount of liquid gave a depth of about 1″ at the deepest point and its surface had a width of 4″ throughout the length of the bottle, i. e., about 6.5″. The bottle was rotated uniformly at 140 r.p.m., imparting a rocker-like motion to the salt particle. The action consisted in the particle periodically rising and sliding down the bottle wall. The bottle was tipped slightly towards the open mouth so that the particle tended to travel from one end to the other. It was inserted and removed by means of a pair of wide-faced tongs without stopping the agitation. After its removal it was immediately dropped into alcohol and washed and dried in the usual manner. Temperature 20° C. The particle weighed 1.0795 g.

TABLE 17. EXPT. 144A.

Ball Mill Type.

Time Min.	Δt Min.	Weight g.	% Diss'd.	$w^{1/3}$	$K_{.5}$ Eq. (8)
0.00	.00	1.0795	0.0	1.0258	——
1.00	1.00	.6945	35.0	.8856	.0701
1.50	.50	.5503	49.0	.8195	.0661
2.45	.95*	.3287	69.5	.6901	.0680
					Mean = .0680
					Ave. D/M = 1.9%

Note—* 57 sec. General shape about the same with some rounding. Concentration changes negligible, .75 g. in 250 cc.

Expt. 144B.

Conditions—Same as Expt. 144A.

Method and Apparatus. Same as before but instead of water used a 50% Satd. salt solution (250 cc. of water plus 44.9 g. of salt).

TABLE 18. EXPT. 144B.

Ball Mill Type. 50% Satd. Salt Solution.

Time Min.	Δt Min.	Weight g.	% Diss'd.	$w^{1/3}$	K_1 Eq. (8)
0.00	0.00	1.2165	0.0	1.0675	------
1.00	1.00	1.1800	2.9	1.0567	.0108
5.50	4.50	1.0319	15.1	1.0105	.0103
7.50	2.00	.9710	20.2	.9902	.0101
10.75	3.25	.8780	31.8	.9575	.0101
14.91	4.16	.7703	36.8	.9167	.0098

Mean = .0102
Ave. D/M = 2.5%

Note—There was considerable movement by the particle from one end of the bottle to the other in this experiment with a tendency for it to stay in the inner end. This prevented the choice of any particular time interval because the opportunity had to be awaited for the particle to come to the front so that it could be removed. The change in concentration was negligible as before.

The slowing up of the rate when B is compared to A, due to the increased concentration in B may be noted in the constants. No further experiments were made in this type of agitation on account of the manipulative difficulties of the apparatus.

6. Conclusions.

The results obtained in this group of experiments on other types of agitation show definitely that the application of the law to dissolution is independent of the type of motion producing the agitation.

OTHER AGITATION SYSTEMS.

1. Solid-Gas System.

Expt. 134.

Conditions—Irregular Naphthalene Particles. Moist Air at 65° C. Dry Bulb (D.B.), 49° C. Wet Bulb (W.B.) and 43% Relative Humidity (R.H.). Carrier Air Conditioning Equipment.

Method and Apparatus. The Carrier Standard Processing Cabinet (2′x2.5′x4′) was used to obtain an automatically regu-

lated supply of gas (air) having a constant temperature and composition. The circulation in this cabinet is stated to be about 400 cubic feet of air per minute with an approximate linear velocity of 100 feet per minute. Room conditions were 26° C., D.B., 19° C., W.B. and R.H. = 50%.*

After the cabinet had reached equilibrium under the conditions chosen for the experiment the naphthalene particles were emptied from the weighing bottle on to a small tinned plate and quickly placed on the lower shelf of the cabinet. At the end of the period they were removed and emptied into the weighing bottle and weighed as rapidly as possible. They were then replaced in the cabinet for the next period. In the meantime, the small amount of naphthalene that had sublimed while the particles were in the weighing bottle was weighed and the gross weight corrected for this amount (usually 1-3 mg.). As usual, all of these operations were well standardized by practice. It was found possible to control the humidity within a range of 2-3% and the dry bulb temperature within 1° C. The naphthalene consisted of 32 irregular shaped particles of fairly uniform size (unscreened) which had been well rinsed with alcohol and examined for possible fractures, cracks and other irregularities. Weight, 6.7468 g.

TABLE 19. EXPT. 134.

Solid—Gas System (1).

65° C. — 43% R. H.

Time Min.	Δt Min.	W.B. °C.	D.B. °C.	Weight g.	% Diss'd.	$w^{1/4}$	K_{20} Eq.(8)
0	0	51.0	65.0	6.7468	0.0	1.8895	———
20	20	49.0	65.0	5.3398	20.7	1.7478	.1417
40	20	48.5	65.0	4.3291	35.8	1.6298	.1180
60	20	49.0	65.0	3.3173	50.5	1.4914	.1384
81	21	47.5	65.5	2.4621	63.5	1.3503	.1344

Mean = .1331

Ave. D/M = 5.6%

Note—There was considerable variation in shape during the run.

* The Bulkeley Chart published by the American Society of Heating and Ventilating Engineers was employed for the humidity data which are reported in these experiments.

Expt. 136A.

Conditions—Irregular Naphthalene Particles. Moist Air at 65° C., D.B., 49° C., W.B. and R.H. = 55%. Same equipment as before.

Method and Apparatus. Same as for Expt. 134 except the naphthalene used was 210 irregular shaped particles which had been well examined, washed with alcohol and dried after which they were carrefully screened to give a 3-4 mesh Tyler screen cut. They weighed 19.8208 g. Operation the same as before. Room Conditions: 25° C., D.B., 19° C., W.B. and R.H. = 55%.

TABLE 20. EXPT. 136A.

Solid—Gas System (2).

65° C. — 55% R. H.

Time Min.	Δt Min.	Weight g.	% Diss'd.	$w^{1/3}$	K_{15} Eq. (8)
0	0	19.8208	0.0	2.7063	———
15	15	17.4833	11.8	2.5954	.1109
30	15	15.3348	22.6	2.4844	.1110
45	15	13.1588	33.7	2.3609	.1235
60	15	11.4589	42.2	2.2545	.1064
75	15	9.9778	50.0	2.1528	.1017
105	30	6.9031	65.4	1.9041	.1243
135	30	4.0829	79.6	1.5983	.1529*

Mean (*omitted) = .1129
Ave. D/M = 6.3%

Note—The final particles showed a considerable variation from the original ones in shape. However up to 50% dissolved the constant shows that the action is normal. The mean value of the constant calculated up to the point of 50% dissolved is .1107 with an Ave. D/M = 4.8% which is quite satisfactory for this kind of work.

Expt. 137A.

Conditions—Irregular Naphthalene Particles. Moist Air at 65° C.D.B., 34° C.W.B. and R.H. = 13%.

Method and Apparatus. Same as before except the naphthalene used was 30 particles of a 3-4 mash screen cut and weighed 3.4579 g. Room Conditions: 28.5° C., D.B., 19.5° C., W.B. and R. H. = 43%.

TABLE 21. EXPT. 137A.

Solid—Gas System (3).

65° C.—13% R. H.

Time Min.	Δt Min.	Weight g.	% Diss'd.	$w^{1/3}$	K_{15} Eq. (8)
0	0	3.4579	0.0	1.5122	———
15	15	2.8753	16.8	1.4220	.0902
30	15	2.3564	31.8	1.3307	.0913
45	15	1.8689	45.7	1.2318	.0989
60	15	1.4889	56.7	1.1419	.0899
80	20	1.0095	70.5	1.0032	.1038

Mean = .0948

Ave. D/M = 5.6%

Expt. 137B.

Conditions—Regular Shaped Naphthalene Balls. Other Conditions as in Part A.

Method and Apparatus. Same as in Expt. 137A since it was run simultaneously with that experiment. Six regular sized naphthalene balls were well washed with alcohol then dried and weighed. Weight, 23.1529 g. They were placed in the cabinet on a paper plate.

TABLE 22. EXPT. 137B.

Solid—Gas System (4).

Heat Effect. 65° C.—13% R. H.

Time Min.	Δt Min.	Weight g.	% Diss'd.	$w^{1/3}$	K_{15} Eq. (8)
0	0	23.1529	0.0	2.8502	———
15	15	22.2656	3.9	2.8133	.0369
30	15	21.3352	7.8	2.7735	.0398
45	15	20.4010	11.8	2.7324	.0411
60	15	19.5822	15.4	2.6954	.0370
80	20	18.3116	20.9	2.6358	.0447
110	30	16.5038	28.8	2.5460	.0447
140	30	14.8121	36.0	2.4559	.0450
155	15	14.0056	39.5	2.4105	.0454

Here the value of K increases from the start and does not begin to show any tendency to become constant until after the first three or four periods. This fact suggested the possibility that it was requiring this length of time for these larger particles to be

heated from the room temperature of 28.5° C. on the outside of the cabinet up to a temperature of 65° C. on the inside. They were also undergoing the cooling process of sublimation at the same time. Therefore, in order to test out this possibility it was decided to make another run with the cabinet dry bulb temperature the same as that of the room. In this case the warming-up period would not be present and the value of the constant should not show this variation at the start of the experiment.

Expt. 138.

Conditions—Regular Shaped Naphthalene Balls. Moist Air at 25° C., D.B., 17.5° C., W.B. and R.H. = 49%.

Method and Apparatus. Room conditions the same as those of the cabinet. Six of the same kind of naphthalene balls were prepared as in the last experiment. Their weight was 23.7225 g.

TABLE 23. EXPT. 138.

Solid—Gas System (5).

25° C. — 49% R. H.

Time Min.	Δt Min.	Weight g.	$w^{1/3}$	K_{30} Eq. (8)
0	0	23.7225	2.8733	——
31	31	23.6445	2.8702	.0030
61	30	23.5672	2.8671	.0031
86	25	23.5062	2.8646	.0030
146	60	23.3552	2.8584	.0031
206	60	23.2104	2.8525	.0029
266	60	23.0577	2.8462	.0031

Mean = .0030

Ave. D/M = 2.7%

Note—At this low temperature the rate was slow as would be expected, less than three per cent of the naphthalene subliming.

Judging from the values of the constant obtained, the explanation which was suggested is probably the correct one.

2. Solid-Solid System.

When the analogy of dissolution is carried over into this system, the experiments become those in which grinding by abra-

sion occurs (breaking by impact or crushing are excluded).* In such experiments, many of those factors which were either negligible or had relatively small effects in the other systems previously studied, now become highly important. One of these is the relative hardness of the materials comprising the system. Another is the question of the different rates at which abrasion takes place in different directions through the particle for this is a constant force which is acting to determine a particular shape. This causes a definite trend in the total observed abrasion which is reflected in the value of the calculated constant. Again, the rate is usually quite slow (e. g. in a ball mill) so that the experiments require a great deal of time. In view of these facts, it is evident that a fair test of the law would require that the following conditions be fulfilled:

(a) A quite hard abrading agent which would be present as rather small-sized particles whose own rate of abrasion (i. e. by itself) would be relatively low.

(b) A softer material present in larger particles than the above whose rate of abrasion by the particles of the other solid would be relatively high.

(c)) The softer solid would have to wear or grind at the same rate along all of its axes (i. e. be isotropic).

In that portion of the time that was available for this part of the research, it was found to be too difficult a matter to meet all of these conditions, but several experiments were contrived whose results indicated that we were on the right track.

In the experiments mentioned, selenite (crystalline $CaSO_4$. $2H_2O$) and quartz particles were rotated in a porcelain jar mill for definite time periods. The softer selenite particles were weighed after each interval and their loss in weight determined. "Cushioning" was avoided by screening and air-blowing to remove all the fine material which was produced each period. Selenite has a very definite crystalline structure and cleaves very easily. It was apparent that it was abraded faster in some directions than in others. The total amount abraded was quite small

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* See p. 70.

in all cases amounting to between four and ten per cent of the initial weights over a total grinding time of twelve hours. However, the constants calculated from Eq(8) showed an Ave. D/M of less than 4%, a fact which seemed to indicate that with the proper precautions the law could be shown to hold. Enough was done to indicate that many of the difficulties that were met with could be overcome in a more extended study.. On the basis of what has been done it is felt that the scope of the investigation does not warrant the drawing of a conclusion. This was an extremely interesting field and further experimentation was postponed with much reluctance.

3. Solid-Liquid Chemical Systems.

These experiments will show what happens when a particle dissolves in a liquid with which it reacts to form a precipitate that is deposited on the surface of the solid as a protective coating tending to prevent the further solution of the solid. The first experiment shows that the action is normal provided the agitation is sufficiently intense so that it removes the coating as fast as it is formed. The second experiment shows that if the agitation is not intense enough to do this, the reaction is slowed down depending on the length of the time interval or the thickness of the protective coating.

Expt. 161.

Conditions—Irregular Alum Particle. Aqueous Ammonia. Free Rotational Agitation.

Method and Apparatus. 4.1. Pyrex beaker, standard straight iron paddle agitator 3″ long and 1″ wide, set at .5″ off of the bottom at the center and running at 291 r.p.m. 2000 cc. of water were used to which were added 50 cc. of concentrated ammonia (Sp. Gr. .90) giving a .63% solution. The alum (potash) was an irregular particle weighing .5380 g. It was dropped in with the agitator running but was removed with a pair of wide-faced tongs immediately after stopping the stirring. It moved quite rapidly in the solution and it was impossible to detect the presence of a coating upon it at any time. The hydroxide showed

up in the form of small flakes in the solution. After removal the particle was dropped into alcohol, washed, dried and weighed. The temperature was 16.5° C. throughout the experiment.

TABLE 24. EXPT. 161.

Alum—Ammonia. No Protective Coat.

Time Min.	Δt Min.	Weight g.	% Diss'd.	$w^{1/3}$	K_1 Eq. (8)
0.00	0.00	.5380	0.0	.8133	——
2.00	2.00	.4925	8.4	.7897	.0118
6.00	4.00	.4142	23.0	.7454	.0111
10.16	4.16	.3429	36.2	.6999	.0109
14.26	4.10	.2773	48.3	.6521	.0116
17.26	3.00	.2338	56.5	.6161	.0120

Mean = .0115
Ave. D/M = 3.3%

Expt. 162.

Conditions—Same as in Expt. 161 but use 5% ammonia solution.

Method and Apparatus. Glass crystallizing dish 2″ in diameter. Small glass agitator running at 150 r.p.m. 43.5 cc. of water to which 10 cc. of concentrated ammonia were added to give an approximately 5% solution. Run at room temperature, 21° C. Irregular particle of alum, weight 2.4607 g. The particle was al-

TABLE 25. EXPT. 162.

Alum—Ammonia. Protective Coat.

Δt Min.	Weight g.	% Diss'd.	$w^{1/3}$	K_1 Eq. (8)	
0	2.4607	0.0	1.3500	——	
4	2.2289	9.3	1.3062	.0109 b	
2	2.0790	15.4	1.2763	.0149 a	
4	1.8860	23.2	1.2355	.0102 b	(1)
4	1.7050	30.6	1.1946	.0102 b	
2	1.5896	35.3	1.1671	.0137 a	(2)
2	1.4742	40.0	1.1381	.0145 a	
4	1.3252	46.1	1.0984	.0099 b	
8	1.1370	53.8	1.0437	.0069 c	(3)
2	1.0462	57.4	1.0151	.0143 a	
4	.9368	61.8	.9784	.0092 b	(4)

Note—(1) Cracks appear in the coating in the same places each time and leave corresponding indentations on the particle's surface. (2) One-half minute on a different side. (3) Crack in the coat became about 1 mm. wide by the end of the period. (4) Particle slightly flatter on the lower side, other sides and edges sharp and same as in original.

Throughout the entire run it was observed that on the leeward side of the particle, density waves or striations occurred indicating that some kind of a solution or liquid was coming through the coating into the main solution. This material did not form a precipitate with the ammonia so it was probably the potassium sulfate solution formed from the decomposition of the alum and which was passing out into the solution. (a) =2 Min., (b) = 4 Min. and (c) = 8 Min. Periods.

ways placed in the same spot and lay on the same side. It was not moved by the agitation. Inserted and removed with the agitator stopped. Due to the shallowness of the container these operations required only 2-3 seconds so that their effect upon the total time period is negligible. After removal the particle was thrown into alcohol and its coating was immediately washed off after which it was dried and weighed.

The dependence of the value of the constant upon the time interval substantiates the statements made before as there are here three distinct values for the constant, viz. (a) = .0143, (b) = .0101 and (c) =.0069 showing that the reaction slows down as the coating gets thicker. The cracking of the coating at the same spots each time within a few seconds after insertion was evidently due to the pressure caused by the increasing precipitate forming below it. Their position probably depended upon the initial shape of the particle and the way the coating reacted to relieve the strain .

In the first experiment the constant did not depend on the length of the period. In the second experiment it did. This is additional evidence that the thickness of the coating regulated the speed of the reaction during each time interval.

4. Comment and Conclusions.

Concerning the application of the law to other systems, enough has been presented to show that there is a great deal of interesting research to be done. Also, that the utmost caution is necessary in the experimental work in each system. For one must

be careful in the substitution of experimental values in the equations that the conditions under which the values were obtained were the same as those which are demanded by the equations. It is again recalled that this law expresses a rigid mathematical relation between the velocity of transformation and the surface and concentration factors only. All of the other numerous factors that affect this velocity are required by the equation to be held constant. Naturally, the relative importance of these factors varies greatly in passing from one system to another. For example, in the solid-liquid dissolution system which was used for the main study, the most disturbing factors were the shape and specific surface of the solid particle, while the disturbing influences of temperature and heat transfer were not so important. On the other hand, in the solid-gas system these latter factors became quite important when the size of the particle was increased. In the solid-solid system such disturbing factors as relative hardness, cushioning and directional abrasion appear. Likewise in the solid-liquid chemical system which was studied, the agitation and the protective coating have great effects on the question of whether the law is applicable. In each case it is a question whether the conditions demanded by the equation have been fulfilled. Each system, therefore, has according to its nature, certain factors whose constancy can be obtained only with difficulty.

If then, it is assumed that all of the other factors except concentration and surface can be held constant in any given agitation system, what kind of transformations may properly be considered. The law (especially Eq. (8)), should be operative in those transformations where the size of the particle, drop or bubble* decreases with the time as the reaction proceeds. This, of course, is on the assumption that the rate at which the transformation proceeds is proportional to the surface exposed.

Theoretically, the law should also be applicable in the other alternative (where the size increases with time), but we have not progressed far enough to obtain any information on this point.

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* Since in a gas-gas system a "gas bubble" does not have a well-defined surface, this system is not included.

In the first class, we ought to find such operations as the dissolution of solids, liquids and gases, evaporation, sublimation and abrasion. In the second class we might find such possible operations as agglomeration, condensation and crystallization. In both cases the terms used are to be taken in their most general sense. A helpful classification of such processes, based upon diffusion as the prime operating force, is given by Walker, Lewis and McAdams in their textbook,[47] where the mechanism of the adhering surface film is stressed.

With respect to the surface film principle, it can be said that there is no disagreement between that viewpoint and the one that has been here formulated. Here, the force residing in the system due to its being at a distance from the final equilibrium is considered as the prime operating force, regardless of whether that equilibrium is momentarily and continually set up in a surface film or whether it is regarded as eventually and completely set up throughout the entire volume.

Returning to the matter of experimentation in the above-considered systems, one may expect that the experimental difficulties will vary greatly depending on the sensitivity of the law towards those factors which it is necessary to keep constant in order to show its applicability. The effect of the variation in some of these factors is shown in the next section.

After the completion of the experimental work that is presented in this thesis and during the collation of its results, an article was encountered in which the derivation and verification of Eq. (8) was reported.[48] This was in connection with a solid-solid system in the study of several auto-catalytic reactions. The thermal decomposition of several compounds was studied, one for example, being potassium permanganate. The hypothesis upon which the authors based the derivation of the equation was that the velocity of the reaction was directly proportional to the interfacial contact surface between the decomposition products and the undecomposed permanganate. From this they developed an expression which is identical with Eq. (8). Their results supported this equation in a very satisfactory manner.

This independent and simultaneous corroboration of the specific application of the Cube Root Law in a type of reactions of

so different a nature from those studied in this research, can only be considered as a strong confirmation of the more generalized viewpoint which has been elaborated in this dissertation.

MISCELLANEOUS DISTURBING FACTORS.

1. Shape Change Effects.

In order to show that a sharp and definite change of shape was associated with a correspondingly sharp and definite change in the value of the constant, the following experiment was devised in which this variable was largely controlled by the imposed conditions.

Conditions—Naphthalene. Alcohol (95%). Free Rotational Agitation.

Method and Apparatus. 600 cc. Pyrex beaker. Standard straight iron paddle agitator 2″ long and 1″ wide set at 1.25″ off of the bottom and running at 82 r.p.m. 500 cc. of alcohol containing 6.062 g. of dissolved naphthalene. Temperature 20° C.

A body having the shape and dimensions shown in Fig. 1 was fashioned out of a naphthalene ball. After carefully sandpapering and filing it down to the dimensions given, it was rinsed well

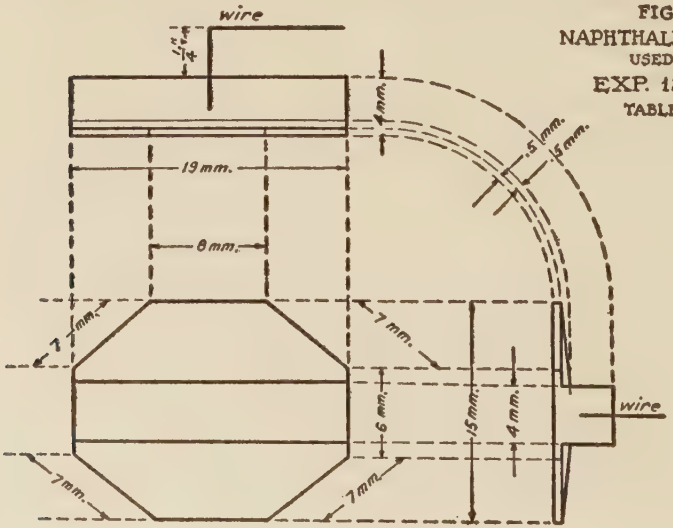

FIG. 1
NAPHTHALENE BODY
USED IN
EXP. 120 C
TABLE 26

in alcohol, dried and weighed. Its weight was .6762 g. The wire weighed .1847 g. It was fastened securely to a glass tube so that the particle could be lowered to exactly the same position in the liquid for each time interval. It was also arranged so that the time required for the insertion and removal was not over three or four seconds. After its removal the particle was immediately dried with a filter paper, given a light blast of air, placed in a weighing bottle and weighed. The position it occupied in the liquid was near the top with the horizontal bend of the wire .75″ from the wall of the beaker and .87″ below the surface. Its broad, flat plate was normal to the stream with its plane lying along a radius. Insertion and removal without stopping the agitator. An effort was made to arrange the time periods so that the change where the shield suddenly changed into the rod would come entirely in one period. That this effort was partially successful, the remarks given will show.

TABLE 26. EXPT. 120C.

Effect of Change of Shape.

Time Min.	Δt Min.	Weight g.	% Diss'd.	$w^{1/3}$	K_1 Eq. (8)
0.0	0.0	.6762	0.0	.87772	.....
4.0	4.0	.5149	23.8	.80151	.01905 (1)
6.5	2.5	.4230	37.5	.75067	.02033 (2)
11.5	5.0	.2821	58.3	.65584	.01896 (3)
14.5	3.0	.2254	66.7	.60858	.01575 (4)
21.5	7.0	.1289	81.0	.50514	.01477 (5)

(1) Edge very thin (estimated as .2 mm.). No crumbling of any kind and only very slight serrations. No holes.

(2) Plate paper—thin at edges, no shape change or crumbling. 15 mm. wide by 18.5 mm. long.

(3) At two minutes, one very small airhole (?) uncovered. Very rapid change the last minute of this period. Very slight serrations. At the end of this period the plate was almost a perfect ellipse, 8 x 18 mm. No holes or cracks at any time.

(4) Practically all of the outer plate gone except a thin narrow fringe. Total thickness through the rod was 3 mm. Rear edges of the rod were well rounded and it was becoming pitted at the rear in the center around the place where the wire entered.

(5) 17.5 mm. long and 3 mm. wide by 2.5 mm. thick. Edges and ends well rounded. No plate, no pits, no holes. Merely a rod.

Note—Concentration change from 23.1 to 25.2% Satd. = 2.1%. Total area change from 6.25 cm.^{2} to 2.25 cm.^{2} (approx.) = 4.0 cm.^{2}

The average of the first two values of K or .01969 may be taken as the constant for the original figure and the last value as that for the final rod-like figure while the other values show the fast change in K due to the rapidly changing shape and specific surface. Attention is directed to the particularly large change in the value of the constant during the fourth interval where the shape was changing so rapidly. Other examples of this effect were pointed out in the experiments on pp. 42, 43.

During the experiment the plate was watched very closely in order to discover as much about its texture as possible. It was observed that there was no crumbling, hole formation, cracking or any irregularity of that nature regardless of how thin the section became and even at its thinnest it still presented the appearance of a delicate mosaic. Therefore as far as the action of these balls towards dissolving in liquids is concerned, it would seem proper to consider them as isotropic bodies.

2. Agitation Effects.

The effect of a change in agitation during the experiment was pointed out on p. 43 in connection with Tables 2-3. The example given below occurred accidentally and illustrates the care that has to be exercised in work of this kind.

Conditions—Irregular Salt Particle. Water. Free Rotational Agitation.

Method and Apparatus. 4.1. Pyrex beaker. 2000 g. of water at 20° C. Standard straight iron paddle agitator 3.75″ long and 1″ wide, set at .5″ off of the bottom and running at 81 r.p.m. Particle inserted by dropping it in 1″ from the agitator shaft while stirring. Stop to remove in the usual manner. After its removal the particle was treated with alcohol in the ordinary way. Weight of the salt particle taken was 1.3085 g.

TABLE 27. EXPT. 124A.

Effect of Change in Agitation.

Time Min.	Δt Min.	Weight g.	% Diss'd.	$w^{\frac{1}{3}}$	$K_{.5}$ Eq. (8)
0.00	.00	1.3085	0.0	1.0928	------
.50	.50	1.1479	12.3	1.0471	.0457 (1)
1.05	.55	.9948	24.0	.9983	.0444
1.55	.50	.8656	33.9	.9530	.0453 (2)
2.05	.50	.7373	43.7	.9034	.0496 (3)
2.55	.50	.6443	50.7	.8637	.0397 (4)

(1) The particle went around twice then went to the center of the beaker and did not move thereafter.

(2) Slightly rounded edges.

(3) Dropped the particle in near the beaker wall by mistake. It continued to circle around for the first fifteen seconds before going to the center. Edges more rounded.

(4) Dropped the particle in at the original place and it acted as usual. Its final shape was considerably more rounded than before.

Note—Concentration change negligible. Mean K for the first three periods was .0451 with an Ave. D/M of 1.1%.

The action during the first three periods is normal but the slight excess agitation that the particle received in the fourth period is reflected at once in the constant. Another result of this happening is to change the shape also so that the last period shows a lower rate than normal even with the same agitation as at the beginning. This shows how sensitive the rate of solution is towards any increase in the intensity of the agitation. The influence of changed agitational conditions frequently appears near the end of a dissolution when the particle has become so small that it moves into a region of a higher intensity of agitation.

3. Disappearance of Particles.

If a large number of small particles are mixed with a smaller number of larger particles and the combination is subjected to the process of dissolution the rate of the mixture will at first be very rapid until all of the small particles have disappeared. The rate will then decrease to that of the larger ones alone in that concentration of solution. Therefore, when comparative experiments are made, it is inadvisable to have such a variation in size

or to run the experiment so far that there will be a material change in the number of the particles. With screened products of the character that have been used in this work, it is quite safe to make comparisons over a range of the first 50% of the material dissolved as the change in the number of particles can then be considered negligible.

PRECISION OF RESULTS

In the case of the ordinary dissolution of a solid, it has been seen that the values of the constants generally show an average D/M of 1-4%. If however, only the first half of the dissolution is considered, it will be found that in many cases the agreement is still better. In general, it is felt that it is advisable to restrict the study to this range of the action due to the difficulties involved in changes of shape (especially in the case of a solid).

On the other hand, it is not believed that this decision in any sense acts to invalidate the application of the law for the remainder of the range of action. The work done in other systems indicates that a precision of practically the same magnitude is easily obtainable.

B. THE STUDY OF AGITATION.

Explanation of the Method.

The only type of agitation that will be studied with respect to the different factors which affect its intensity is the free rotational type. This type was chosen on account of its inherent simplicity and the ease with which modifications could be introduced into the apparatus so as to allow the study of a single variable at a time. In this respect it was thought best to set up a standard set of conditions or agitations in this type so that whenever it was desired to study the effect of a variable, all that would be necessary would be to make a small change in the apparatus of the standard. The rate of dissolution would then be measured and the result compared with the standard in order to show the effect of the variation in so far as it acted to change the intensity of the agitation.

Since the character of the agitation varies with the speed of the agitator, certain speeds were chosen as generally represent-

ing the various characteristic regimes of agitation and in certain cases these were used for comparative purposes. Whenever it was possible to calculate a value for the constant according to Eq. (8), this was done, for whenever equal weights of the same solid and equal volumes of the same solvent are used, the rates of dissolution vary directly as the constants. In those cases where the agitation was so low that stagnation and slow distribution prevented the law from operating so that a constant could not be calculated, other means of comparison had to be sought. In one method the respective times required to reach the same concentration of the dissolved solid (say one-half of the final value) could be compared. However, most industrial agitations are of such an intensity that they may be studied by the use of the constant. Therefore, but little time was devoted to the study of other methods.

The first section describes the apparatus forming the "standard" agitation set-up of the free rotational type. The second describes some of the characteristics of the various regimes of agitation encountered and the third considers the experiments concerning the different variations made in the standard.

STANDARD AGITATIONS.

1. General Purposes.

While many considerations entered into the choice of the final apparatus, those of convenience, simplicity and availability were thought to be the most important. In the first place it was desired to construct the container and agitators out of ordinary laboratory apparatus so that an agitation could be quickly set up by anyone and run with the assurance that the intensity that they were obtaining was the same as that obtained by anyone else using the same standard.

2. Apparatus and Methods.*

(a) **Container.** An ordinary four liter Pyrex beaker, 6″ in diameter and 9″ deep. Several different ones were tried and no

* This set-up in its entirety was used in Expt. 53 Table 6, p. 46.

difference between them was found so they were considered uniform enough to be specified for this purpose.

(b) **Agitators.** The standard agitator chosen as that one from which the variations into the other kinds could be made most readily was the simple paddle with straight blades. The material was iron and the shaft was straight .25″ soft iron of circular cross section, obtainable in any machine shop. Its length was a matter of choice but it was found that an overall length of 11″ was quite satisfactory for the majority of cases. The blades were composed of one piece of flat rectangular-shaped 18 gauge (B. & S.) sheet iron, 1″ wide and 4.25″ long. This was fitted into the shaft in the following manner. An ordinary hacksaw cut of 1″ depth was made in the end of the shaft. The central part of the blade fitted snugly into this cut so that its lower edge was flush with the sawed-off end of the shaft. It was fastened in position either by two small rivets or more often by the use of a small amount of solder. All jagged edges, bumps or irregularities were filed down to give a clean, flat and regular surface. This gave a total blade surface of 4 in^2 (one side only).

(c) **Position of the Agitator.** The agitator was set in the center of the beaker and at a height of .5″ up from the bottom. Since the bottoms of these beakers are slightly raised in the center (.12″ approx.), this fact must be considered. The top of this raised portion is regarded as the bottom of the beaker wherever this measurement is mentioned.

(d) **The Liquid.** Two thousand grams of ordinary city tap water were used. It should be pure enough for drinking purposes and any amount of dissolved solids or insolubles it might contain should be negligible.

(e) **Temperature.** The standard temperature chosen was 20° C., taken at the beginning and maintained throughout the run, if the time of the run was of appreciable length. If the total amount of the salt was dissolved the temperature would be lowered about .5° C., but as the determination was usually made at a time before all of the salt had dissolved, the temperature change

can be neglected. In this respect, the procedure has followed that of other workers who have used salt and water for these purposes. As a matter of fact, the change in solubility of NaCl with the temperature is so slight that this seems quite justifiable.

(f) **The Solid.** The standard solid used was obtained by screening a naturally-mined crushed rock salt.* Except for a few isolated runs which were made on samples screened at different times, all of the work on agitation was carried out using the same material, i. e. portions of a lot weighing about ninety pounds which had been screened all at one time. As this screening operation is quite important, its details will be described.

About 200 lbs. of the original material were screened by hand with a 4 mesh Tyler Standard sieve. The oversize from this operation was then screened twice on a mechanical shaking screen using a 3 mesh Tyler Standard sieve. The fines from this last operation, together with 2-3 lbs. recovered from a mechanical rescreening of the fines from the hand process, constituted a 3-4 T.S. cut which was used as the standard material. Several isolations of this cut from different bags of the unscreened material showed that it acted uniformly in the process of dissolution and could be expected to give the same results. The amount of this fraction in the original ran about 47-48% by weight.

During the course of this work over 175 lots of 40 g. each of this material were weighed and the number of particles in each one determined by actual count. The average weight of a particle was .2118 g. and the average number of particles per 40 g. was 189 with an average deviation of 7.7 particles or an Ave. D/M of 3.0%. A fairly representative screen analysis upon this material is given in Table 28 below.

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* This material was an "ice-cream salt" purchased from the Independent Salt Co., New York, N. Y., under the name of "Natural Mined Blu-salt No. 1." The most of its particles were about the size of a pea. Samples of similar salt from other companies appeared to have different shape characteristics and while they were just as suitable for comparative purposes, their results should not be compared with those obtained from salt having a different source.

TABLE 28. EXPT. 25A.

Screen Analysis of Salt Used.

Retained on No. ____ mesh T. S. Sieve	Weight g.	Per Cent of Total Wt.
3	80.5	6.90
4	527.7	45.50
6	417.0	35.85
8	60.7	5.20
10	38.3	3.30
14	20.3	1.75
14F	17.7	1.50
Total	1162.2	100.00

This material also contained an insoluble residue of 1.57% consisting largely of silica for which a correction was made in each case. For each of the standard agitations 40 g. of this material were weighed out and used. In order to reduce the effect of variation still further the number of particles in each sample was adjusted so that there were 189 in each case.

(g) **Analysis.** The indirect method of analysis was used whereby the concentration of the dissolved salt was determined. Samples of the solution were dipped out and after standing a short time to allow the silica to settle, were analyzed by evaporation of a weighed portion. The samples were handled in weighing bottles and were evaporated to dryness in an oven at 115-120° C. The analysis was carried out in triplicate and the weight of the dissolved salt in grams per hundred grams of water were reported as a ratio designated as "R."

(h) **Place of Sample.** The sample was always taken from the same spot which was one-half the distance from the center to the wall of the beaker. It was taken with a quick swooping motion so as to cause a minimum amount of disturbance in the liquid.

REGIMES OF AGITATION ENCOUNTERED.

With the standard set-up described above, it was noticed that when the speed of the agitator was progressively increased, cer-

tain characteristic regions appeared in which the nature of the generating forces and the agitation itself seemed to be changed. Within the range of agitator speeds investigated the three following regimes of agitation were clearly recognizable.

1. Passive or Non-Flow. (N.F.)

The particles of the solid remained passive at the points where they fell when dropped into the water and did not move during the most of the time of dissolution. Solution took place largely from the top of the particles so that their shape tended to flatten. This type of flow persisted from no stirring whatever up to about 50 r.p.m. In this regime the formation of layers of different concentration occurs when the agitation very nearly approaches that of diffusion alone, due to the fact that the forces of diffusion begin to predominate over those produced mechanically.

2. Curvilinear Flow. (C.F.)

As the speed of the agitator increased, the salt began to move towards the center at which place it tended to pile up and then move around. The characteristic action of this regime is the motion towards the center. Since the particles tend to move in circular paths about the center parallel to each other, this type of flow may be called the curvilinear type in contrast to the straight line or rectilinear type of flow. As the speed of the agitator was further increased the forces moving the particle in its path reached a maximum and at about 150 r.p.m. they were equalized and finally overcome by the centrifugal component so that a new regime began to appear. In the case of most of the simpler-shaped agitators studied, a typical C.F. regime was obtained with a speed of 83 r.p.m.

3. Turbulent Flow. (T.F.)

Between 150 and 300 r.p.m. (as high as the study went), the centrifugal forces of the rotating water became so great that the particles were forced out from the center and driven upward along the beaker walls in spiral-like paths, which resulted in considerable turbulence. The characteristics of this regime are the motions outward and upward from the center and a general

production of turbulence. A speed of 240 r.p.m. was found to produce a typical T.F. regime under the conditions described.

4. Discussion.

The limits at which these regimes of flow set in overlap each other but the characteristics are quite definite. They were observed with many different types of the simpler straight paddle agitators. The passive regime occurs with very slow agitation and is avoided in industrial work for that very reason. Its study, therefore, does not seem to possess much practical value and accordingly little attention was paid to it. There are, however, many interesting facts of theoretical importance connected with it. Under these conditions the distribution is so slow that the concentration increases in the bottom and a constant for the Cube Root Law is not obtained so that other methods of comparison are necessary. As the other two regimes are very important in an industrial sense the attention has been centered on them.

It is probable that each type of agitation (Tumbler, Impeded, etc.) has its own regimes of flow whose characteristics are dependent on the amount, size and density of the solid used in the agitation as well as the nature of the agitation itself. Therefore, these regimes are not to be taken as indications of absolute forces due to geometrical relationships existing in the apparatus but rather as indications of the forces due to the particular conditions employed. With sand and cold glycerine, for instance, the nature and limits of the regimes would probably be far different from those of salt and water.

STUDY OF THE VARIABLES.

1. Angular Velocity. R.P.M.

Conditions—Standard agitations employed, using different agitator speeds.

Method. After the agitator had been going for a few minutes at a uniform rate of speed (its r.p.m. was taken immediately before and after the run with a speed counter), the salt was thrown in and at the end of one and two minutes, respectively, 50 cc.

samples of the solution were collected and analyzed according to the procedure outlined previously. This operation was repeated with fresh water and another salt sample until at least three separate determinations of the rate had been made. The mean of these results was taken as the value for each minute for that speed of the agitator. The following table shows the results.

TABLE 29. EXPT. 64A.

Angular Velocity.

R.P.M.	R'*	Ave. D/M	K_1† Eq. 8	R'' Obsd.	Ave. D/M	R'' Calcd.	R'' Calcd.—Obsd. / Obsd.
		%	1 Min.	2 Min.	%	2 Min.	%
19	.072	12.1	——	.174	3.8	------	---
34	.441	7.2	(.101)	.956	2.5	(.711)	(25.6)
50	.632	3.0	.151	1.186	.5	1.112	6.2
83	.813	0.6	.204	1.368	1.1	1.364	.3
122	.949	1.1	.247	1.563	.2	1.530	2.1
153	1.043	1.4	.281	1.683	.8	1.635	2.8
181	1.145	2.1	.317	1.766	.2	1.731	1.9
240	1.231	1.1	.350	1.820	.3	1.800	1.1
292	1.310	0.9	.384	1.875	.5	1.855	1.0

Note—*R' = Ratio for the first minute, R'' for the second minute, etc.

† These constants are computed from the values of R and are equal to the Ks calculated from the loss in weight divided by 20⅛ or 2.714. The average w_0 equaled 39.37 g., giving c_0 equal to 1.968 with an Ave. D/M of .17%.

The values for any intermediate points that are desired may be obtained by plotting the given points and reading the values on the curve.

In the lower agitations (N.F. Regime), the low degree of precision is shown by the high value of the Ave. D/M. This is due to the fact that in this regime the velocity of solution depends greatly on the manner in which the salt is scattered and how it lies on the bottom of the beaker. That the distribution also is very irregular is shown by the fact that the calculated and observed ratios for the second minute are widely variant for this region. In other words, the solid and solution are not transported to the top at a rate that conforms to that predicted by the Cube Root Law. However, as the distribution becomes more

effective with the faster agitations, it approaches equality with the dissolution rate and the law begins to hold with a greater degree of accuracy.

For the regime of curvilinear flow, it is interesting to note that the values of K are related to the r.p.m. in an approximately linear manner as the results in Table 30 will show. In a way, this checks the work of Huber and Reid (et al) in showing that there is a region in which this relation may be linear in nature.

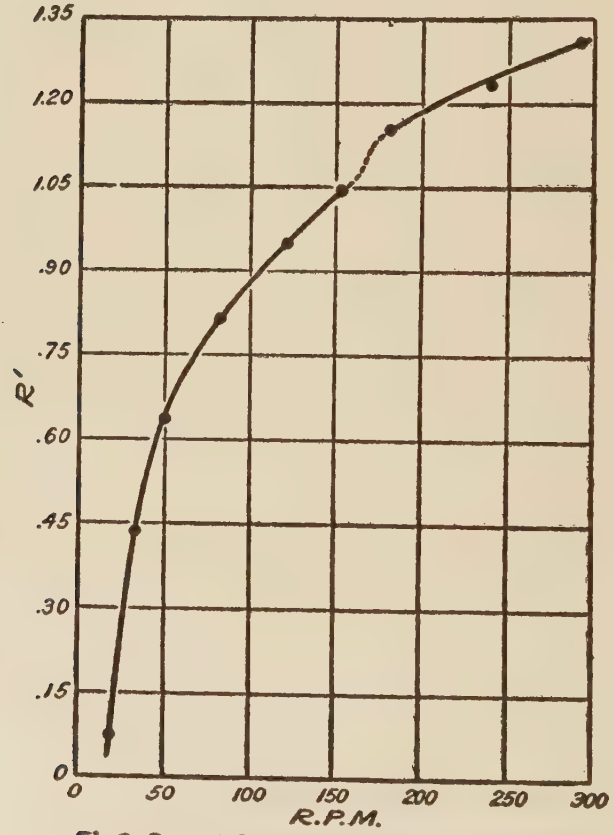

Fig.2-Speed-Concentration Curve. Table 29

TABLE 30. EXPT. 64A.

The Relation of Angular Velocity to the Constants.

From R.P.M.	To R.P.M.	ΔR.P.M.	ΔK	$\frac{\Delta K}{\Delta R.P.M.}$
19	34	15	___	------
34	50	16	.050	.0031
50	83	33	.053	.0016
83	122	39	.043	.0011
122	153	31	.034	.0011
153	181	28	.036	.0013
181	240	59	.033	.0005
240	292	52	.034	.0006

Note—The bars represent the approximate limits of the C. F. regime.

The breaks in the value of the ratio indicate roughly the overlapping limits of the regimes of flow under the conditions here imposed. With a different agitator it is very probable that these limits would be displaced to positions considerably different from the ones shown here. For these reasons, no further attempts will be made to obtain any other empirical relationship between the velocity and the agitator speed. If one could rely on the character of the agitation remaining the same through a longer range of speeds, such a search might be regarded as more profitable. As it stands, it is not profitable to try to draw any conclusions further than those inferred in the discussion on p. 18. It is believed that this subject is too large to be treated in such a simple manner.

Another way of considering the action of the agitator is to calculate the times needed to obtain a concentration of half of the final possible amount. These values are shown in Table 31.

TABLE 31. EXPT. 64A.

Stirrer Performance. Time, R.P.M.

R.P.M.	R′	R″	T_{50}=Time in Min. to give R = .984
34	.441	.956	2.088
50	.632	1.186	1.596
83	.813	1.368	1.261
122	.949	1.563	1.042
153	1.043	1.683	.922
181	1.145	1.766	.818
240	1.231	1.820	.740
292	1.310	1.875	.676

Note—The times were calculated by using Eq. (8) employing the value of the constant obtained from those concentrations in the immediate neighborhood of R = .984.

When these times are plotted against the stirrer rates, a curve is obtained which has the same form as that obtained by Wood, Whittemore and Badger (l.c.) and in fact resembles it so closely that it may be considered as a corroboration of their results for agitation of this type in this region.

2. Size of the Agitator.

Using the same straight paddle agitator that was employed in the standard agitation, its length was varied while its width was held constant and vice versa. All other conditions were the same as those of the standard.

(a) **Width Constant—Length Varying.**

Conditions—All blades were 1″ wide with different lengths. Each length was tested at least in duplicate. Two minute samples only.

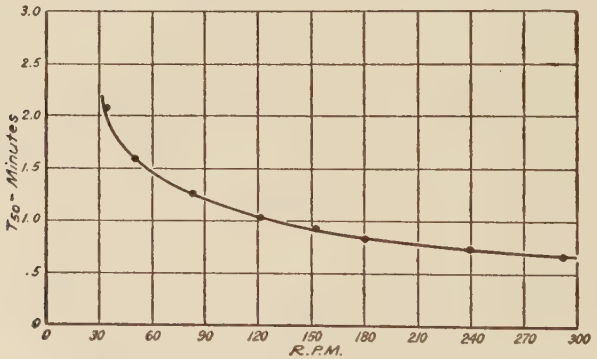

Fig. 3 - Stirrer Performance. Table 31

TABLE 32. EXPTS. 72-76.

Variation in Length of Agitator.

Length* in inches	Per cent of width of beaker	R″	$c_0^{1/3}$	$c_2^{1/4}$	K_1 Eq. (8)
1.00	16.6	.0347	1.254	1.247	.004 N.F.
2.00	33.3	.776	1.254	1.060	.097 C.F.
3.75	62.5	1.353	1.253	.851	.201 "
4.25S	70.7	1.368	1.254	.844	.205 "
4.75	79.0	1.370	1.253	.842	.205 "
5.25	87.5	1.365	1.252	.843	.204 "

Note—* Length given is total over-all length. Beaker is 6″ in diameter. (S) = Standard. Each agitator ran at 83 r.p.m.

Apparently the effect of increased length attains a constant value at about 70% of the diameter of the container.

(b) **Length Constant—Width Varying.**

Conditions—This effect was tested at two speeds. One minute samples. Each agitator was 4.25″ long.

TABLE 33. EXPTS. 74-94.

Variation in Width of Agitator.

Width in inches	R′	$c_0^{1/6}$	$c_1^{1/6}$	K_1 Eq.(8)	R″ Obsd.	R″ Calcd.	Per cent Diff.
			C.F. — 83 R.P.M.				
.50	.725	1.254	1.076	.178	1.271	1.248	1.8
1.00S	.813	1.254	1.050	.204	1.368	1.364	.3
1.50	.855	1.254	1.037	.217	1.420	1.417	.2
			T.F. — 240 R.P.M.				
.50	1.204	1.252	.912	.340	1.781	1.778	.1
1.00S	1.231	1.253	.903	.350	1.820	1.800	1.1
1.50	1.257	1.254	.894	.360	1.821	1.820	Neg.

When the results obtained by changing the width of the agitator in the C.F. regime are compared, it can be seen that the effect is the greatest where the width is the smallest. In the T.F. regime the same increases in width have a relatively less effect upon the value of the constant and it appears to be linear in relation to the width, a circumstance which is probably fortuitous. In both cases the variation was in the direction that was to be expected. Another opportunity was presented here to show the action of the Cube Root Law and the difference between the calculated and observed values of the concentration for the second minute is quite satisfactory.

(c) **Comparison of Different Widths over a Range of Speeds.**

It seemed desirable to make the comparison between two agitators of different widths over a range of speeds which involved both regimes in order to see if the comparison would continue to hold. The .50″ agitator was chosen for this purpose, the length being that of the standard, 4.25″. Two minute samples.

TABLE 34. EXPT. 75.

Variation in R.P.M.—Agitators of Different Widths.

R.P.M.	R″	K_1	R″	K_1	$\frac{K_1(S)}{K_1(.50)}$
	1.00″(S)		.50″		
83	1.368	.205	1.271	.183	1.12
122	1.563	.256	1.484	.234	1.10
153	1.683	.297	1.576	.260	1.14
181	1.766	.335	1.678	.294	1.14

These results show that the comparison of agitators may properly be made through their constants. In this particular case the effects of these two agitators had approximately the same relationship to each other over quite a wide range of speeds.

3. Position of the Agitator—Horizontal.

Variations in the standard agitation were made by placing the stirrer in the beaker eccentrically, i. e. off-center. This was tested for the C.F. regime only. Two minute samples. All at 83 r.p.m.

TABLE 35. EXPT. 69.

Variation in Horizontal Position of the Agitator.

Agitator at inches from center	R″	$c_0^{\frac{1}{6}}$	$c_2^{\frac{1}{6}}$	K_1 Eq.(8)
.00 S	1.368	1.254	.844	.205
.50	1.446	1.253	.805	.224
.75	1.469	1.253	.792	.231

The additional turbulence produced by the agitator when in these positions is at once shown in the value of the constant in the expected manner.

4. Position of the Agitator—Vertical.

On account of the ease with which this variation can be made in practice this variable was tested in both regimes of flow. Variations were made in the height of the standard 1″ agitator. One and two minute samples.

TABLE 36. EXPT. 67-68.

Variation in Vertical Position of the Agitator.

Agitator height inches*	R″	$c_o^{1/8}$	$c_2^{1/8}$	K_1 Eq.(8)
		C.F. — 83 r.p.m.		
.25	1.391	1.254	.833	.211
.50 S	1.368	1.254	.844	.205
1.00	1.351	1.253	.851	.201
2.00	1.359	1.252	.846	.202
2.50	1.373	1.252	.839	.206
		T.F. — 240 r.p.m.		
	(R′)		$(c_1^{1/8})$	
.25	1.272	1.254	.887	.367
.50 S	1.226	1.254	.904	.350
1.00	1.216	1.253	.910	.343
2.00	1.221	1.254	.908	.346
2.50	1.222	1.253	.907	.346

Note—* From the bottom. Excepting .25″ in the C. F. regime the remaining runs in that regime were run in quadruplicate. All other values are averages of duplicate or triplicate runs.

In both cases the constant seems to be higher at the bottom and then to grow smaller as the agitator recedes upwards. Both regimes show that the differences are slight in comparison with the height changes of the agitator. It is likely that a more complete investigation would disclose a gradual decrease in the value of the constant from the bottom upward with possibly a region of very little change in the zone where the agitator passes through the center of inertia of the rotating liquid.

5. Temperature.

Although this variable acts in an indirect manner and is excluded in the usual case, several rates were determined at different temperatures in order to obtain the temperature coefficient of the dissolution reaction. The standard apparatus was used in each case and duplicate runs were made. All at 83 r.p.m.

TABLE 37. EXPT. 70.

Variation in Temperature.

Temp. ° C.	R″	$c_0^{1/4}$	$c_2^{1/4}$	K_1 Eq.(8)
15	1.258	1.254	.893	.180
20 S	1.368	1.254	.844	.205
25	1.477	1.254	.790	.232
35	1.663	1.254	.677	.288

Note—The temperature coefficients for a ten degree rise are: (15°—25°), 1.28; (25°—35°), 1.24; Average, 1.26.

These results for the temperature coefficients are of the same order as those for many of the heterogeneous reactions reported in the literature,, i. e. between 1.10 and 1.50.

6. Shape of the Vessel.

In this section a few of the more extreme types of geometrical shapes were tested in order to show the variation due to this factor. The standard agitation chosen was that of 122 r.p.m. and the only variant factor was that of the shape of the vessel.

TABLE 38. EXPT. 38.

Variation in Shape of the Vessel.

Description	Depth of water in inches	R″	K_1 Eq.(8)
1. Two liter Pyrex beaker, 5″ diameter	6.25	1.506	.241
2. Four liter Pyrex beaker, 6″ diameter (S)	4.25	1.563	.256
3. Cylindrical copper can, 9″ diameter	1.87	1.642	.283
4. Square tin can, 5″ x 5″ *	5.00	1.551	.253

Note—All were C. F. regimes. * The corners were rounded off in quadrants of a circle of .25″ radius and acted like breakers forming four distinct vortices. In case No. 3 the top of the water was but .375″ above the top of the agitator and this probably accounts for the fast rate.

The difference in height very likely contributes a large share to the variations observed in these cases, although the effect of the corners in the square can is obviously toward more turbulency even if it is more or less localized in action. These experiments were presented largely to show the magnitude of the deviations from the standard.

7. Shape of the Agitator.

This is one of the most important of the variables to be considered and in general it is one of the most difficult to classify due to the extreme variability of the modifications that appear in practical use. All that can be done here is to test a few of the simpler types.

In all cases the total, overall, straight-line diameter was the same as that of the standard or 4.25″. All of the blades were made from 18 gauge (B&S) galvanized sheet iron. The shafts were made of .25″ round soft iron. These materials are the same as those described in the making of the standard set-up on p. 78.

(a) **A-Shaped Type.**

A simple straight paddle agitator .50″ wide was provided with two sheet iron braces each .25″ wide, which ran from the ends of the agitator blades to opposite sides of the shaft. These braces were set at a 45° angle to the shaft and blade and were cut to fit flush with the ends of the blades. They were each soldered into position. See Fig. 4a.

(b) **Single Post Gate Type.**

Two pieces of sheet iron (one for each end), .25″ x 1.5″ were soldered perpendicularly to the ends of the blades of a .5″ straight paddle agitator. Each piece or post projected upward 1″ above the top of the .5″ blade and was flush with the end. This agitator is more easily constructed by cutting it out of one piece of sheet iron and the one used in the test was made by this method. See Fig. 4b.

(c) **Multiple Post Gate or Fence Type.**

This was constructed by cutting out four rectangular sections from an ordinary 1.5″ x 4.25″ straight paddle agitator. Each section that was cut out was .25″ wide and 1″ long and they were spaced at .25″ intervals with each other and the shaft so that the final shape resembled that of a picket fence and only differed from the single post type in that it had three extra posts on each blade. See Fig. 4c.

(d) **Four--Bladed Paddle.**

Two blades, each 1″ x 4.25″ were set at right angles to each other on the bottom of the shaft in the manner described before in connection with the construction of the standard two-bladed straight paddle agitator in the standard set-up on p. ?? See Fig. 4d.

(e) **Spiral Paddle.**

A strip of sheet iron was bent into a symmetrical S-shaped curve with each blade having a surface generated by the translation of a logarithmic spiral.* See Fig. 4e.

The surface of this agitator has the property such that when it is rotated, a particle striking it is deflected along the radius of the circle of rotation, provided there is no slipping or rolling of the particle on the surface. This curve was tried in order to see if this effect would be noticeable when compared with the straight paddle.

(f) **Propeller.**

This was a piece of sheet iron cut in the shape of a figure eight with a maximum diameter of 1″ occurring at a distance of 1″ out from the shaft. The shaft was soldered at the crossing point of the peripheral boundaries and the total overall length was as usual, 4.25″. The blades were then twisted each to an angle of 22.5° from the horizontal and their planes made a 45° angle with each other. See Fig. 4f.

(g) **Impeller.**

Three single spiral blades of the kind described in (e) each an inch wide as usual, were prepared and fastened in a vertical position by soldering their edges between two circular pieces of sheet iron each of which was 4.25″ in diameter. These two pieces acted as the top and bottom of the impeller and a circular hole 1″ in diameter was cut through both at the center and including the inner portion of the three spiral blades fastened between them. A shaft was soldered perpendicularly to the top by means

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* The equation of this curve in polar coordinates is $r = e^{\theta}$, where r is in eighths of an inch and θ is in radians.

of two braces of semi-circular cross section, .25″ in diameter. The shaft did not project through the inner hole and its lower end was .5″ above the top casing. In this agitator there were no surfaces which would act to produce a motion with a vertical component. This later statement is also applicable to all of the other agitators described and used with the exception of the propeller. See Fig. 4g.

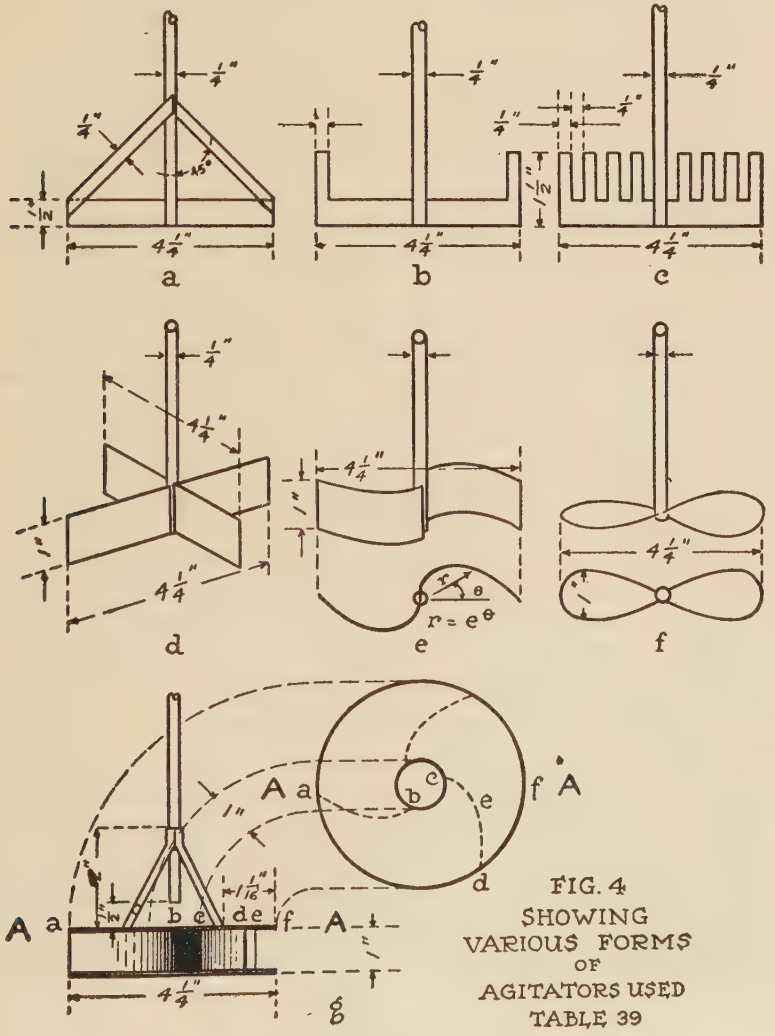

FIG. 4
SHOWING
VARIOUS FORMS
OF
AGITATORS USED
TABLE 39

TABLE 39. EXPTS. 77-90.

Variation in Shape of the Agitator.

Agitator	Name of Type	Width of Blade	K_1 C.F.–83 R.P.M.	K_1 T.F.–240 R.P.M.	Compare with
S-.50	Standard Paddle	.5″	.180	.340	
S-1.0	Standard Paddle	1.0	.204	.350	
S-1.5	Standard Paddle	1.5	.217	.360	
(a)	A-Shaped	.5	.196	351	S–.5
(b)	Single Post Gate	.5	.193	.352	S–.5
(c)	Multiple Post Gate	.5	.202	.356	S–5, (b)
(d)	Four Bladed Paddle	1.0	.209	.365	S–1.0
(e)	Spiral Paddle	1.0	.207	.353	S–1.0
(f)	Propeller	—	.165	.335	S–.5
(g)	Impeller*	1.0	.233	.333	S-1.0, (e)

Note—* For additional experiments on this type see Table 40, p. 95.

Under these conditions of operation certain comparisons are possible and have been indicated. They show how the agitation changes as the shape, area and type of the agitator changes. The effects of some of the changes in construction are nullified at the higher speeds because the vortex produced often uncovers a large portion of the area of the agitator. This was particularly true in (a), (b) and (c). The propeller had very little lifting power due to its relatively low speed, small area and pitch and therefore does not appear in a very advantageous light. The spiral paddle acted practically the same as the simple straight paddle. It is also quite probable that the differences could be made more apparent by changing the reaction conditions but so far the opportunity to demonstrate this has not been afforded.

The case of the impeller is interesting on account of its causing a more efficient agitation in the C.F. regime than the corresponding straight paddle but a less efficient one in the T.F. regime. In order to determine, if possible, at what speed the two agitators were equivalent, it was decided to make the comparison over a range of speeds. The results obtained are given in the table below.

TABLE 40. EXPT. 89.

Comparison of Paddle and Impeller Agitators.

R.P.M.	Depth of Vortex with the Impeller—inches	K_1 Paddle	K_1 Impeller
83	.62	.204	.233
122	1.18	.247	.274
153	1.75	.281	.300
181	2.75*	.317	.316
240	5.12†	.350	.333

Note—* This point is exactly at the entrance of the circular hole in the top of the impeller. † Vortex entirely through the impeller and resting on the bottom of the beaker with considerable air being drawn into the agitator and thrown out through the blades. At this speed the vortex with the paddle agitator just begins to approach the top of the blade.

Evidently, the two agitators become equivalent at about 180 r.p.m. At speeds above this point, the impeller became less efficient than the paddle because it was "pumping" air, an action which is characteristic of this type of agitator. In a case of this kind, unless the vortex is broken up by means of breakers or baffles, this disturbing change in the character of the agitation tends to counteract the effect of increased speed. Before making these quantitative runs whose results have just been given, the apparatus was set up with the impeller and the water alone and the progressive change in the character of the agitation with increasing speed was observed qualitatively. As the speeds were progressively increased through the range shown in the tabulated results, it was observed that when the speed reached the neighborhood of 180 r.p.m. the vortex had been lowered to the top of the agitator and that this was the maximum speed usable without air being drawn into the water. The quantitative result was therefore not entirely unexpected.

This experiment can be regarded as an illustration of the very practical use of this method in the uncovering and elucidation of "trick points" in agitation problems.

8. Volume of the Liquid.

Using the same weights of salt and different volumes of water in the same container and with the same agitator, certain compar-

isons can be made of the effect of the volume upon the intensity of the agitation. The standard apparatus was used with the exception of the agitator which was replaced with the .5″ x 4.25″ paddle agitator used in the other experiments. By using the same weight of salt in each one of a pair of volumes, the effect of its piling together in one heap was avoided. The only comparisons made were those made in the C. F. regime where it was felt that the distribution was rapid enough to permit the calculation of a constant. All runs were made in triplicate.

TABLE 41. EXPT. 99.

Variation in the Volume of the Liquid.

Grams of Salt	Grams of Water	Depth in Inches	R′	K_1 Eq.(8)	Ratio
10	500	1.12	.795	.339*	
10	2000	4.25	.181	.303	
20	1000	2.12	.769	.411	
20	2000	4.25	.363	.384	1.07
40	1000	2.12	1.564	.529†	
40	2000	4.25	.725	.483	1.09

Note—Top of the agitator blade practically at the water level giving a slightly irregular type of regime. † Calculated value for R″ = 1.317, observed value for R″ = 1.308, Difference = .7%. All were run at 83 r.p.m.

It is quite evident that there is a decrease in the intensity of the agitation due to the increased volume of the liquid. For still larger volumes where the law does not hold, due to the low intensity of the agitation, the comparison requires the use of a graphical method to obtain the times needed to reach a 50% concentration.

9. Place of Sample.

When the volume is large and the intensity of the agitation is low, the distribution is not uniform throughout the volume and samples taken simultaneously at different points show different concentrations. Whenever this is the case the sample should be taken from the top as this is the place at which the attainment

of uniform concentration has ordinarily involved the maximum work of distribution and transportation. For practical purposes, one is interested mainly in that portion of the volume where the concentration is the slowest in reaching its maximum and final value. It is from this place that the samples should be taken when the rate of distribution is being determined. It might well be that in some particular case it would be necessary to determine this place but usually one may choose it from a consideration of the geometrical dimensions of the apparatus. For instance, in the free rotational type of agitation, it is well known that the outer portion of the top layer will show a higher concentration than the portion nearer the center. Accordingly, the place of sampling was chosen at one-half the radius as that involving little if any appreciable error.

The following experiment illustrates how, in a large volume, the concentrations of samples taken from different places vary and also shows how increasing the rate of distribution affects the constants which were calculated as if the law were holding.

Method and Apparatus. A cylindrical tin container which was 6″ in diameter and 14″ deep was equipped with a short .5″ tubular exit at a point 1″ from the bottom. The inner part was flush with the inner wall of the can and the total length was about one inch. A short rubber tube closed with a pinchcock was provided to allow the removal of a sample. Two seconds before the time for the colection of the sample, the pinchcock was opened and the more or less stagnant solution in the tube and spout was allowed to run to waste. Without being closed, the tube was then moved so that the solution was saved for a sample at the proper time. Simultaneously with the collection of the sample at the bottom, a sample was dipped from the surface at the usual place. The same procedure was used for the sample at the second minute. Five kilos of water were used with 40 g. of salt. A standard paddle agitator, .5″ x 4.25″ set at the center and .5″ off of the bottom was used inasmuch as a low intensity of agitation was desired. The results are given for three different speeds.

TABLE 42. EXPT. 106.

Variation in Place of Sample.

R.P.M.	R′		K_1		Obsd. R″		Calcd. R″		Difference in % of Obsd.	
	T	B	T	B	T	B	T	B	T	B
83	.221	.375	.095	.177	.451	.549	.397	.610	12.0	11.1
181	.393	.491	.188	.252	.644	.695	.631	.724	2.0	4.2
240	.449	.576	.223	.321	.698	.749	.688	.777	1.4	3.7

Note—T = Top, B = Bottom. The water was 10.75″ deep in the can. Results are from runs made in duplicate with some in triplicate.

The differences in the concentrations of the top and bottom samples show up very plainly. These results show that the predicted values of the concentration for the second minute, made from those of the first minute, are closer to the observed values in the case of the higher speeds. This permits the inference to be made that with still higher speeds the law would hold in the normal manner.

10. Effects due to the Amount of Solid and its Piling Action.

As long as the amount of solid used is relatively small compared to the area of the bottom of the container and to the volume of the liquid used, the effect of piling or heaping is not noticeable. However, when the amount becomes appreciable, this effect appears as a hindering or slowing down of the rate of dissolution. If the same container (a 4 l. beaker) is used the effect of amounts of salt very much greater than 40 g. is to cause this action to appear. On the other hand, with higher speeds and more intense agitation, this action tends to be eliminated.

TABLE 43. EXPTS. 94-99.

Variation in the Amount of Solid. Piling Effects.

Part A.

Expt. No.	Salt g.	Water g.	R′	K_1 Eq.(8)	K_1 times 1.26*	Remarks
99	10	2000	.181	.303	.383	All agitators in Parts A-B
99	20	2000	.363	.384	.484	were straight paddles,
94	40	2000	.725	.483	.608	.5″ x 4.25″, running at 83 r.p.m.
99	80	2000	1.393	.579	-----	

Part B.								
102	40	4000	.342	.451	.568			
94	80	4000	.642	.527	-----			
Part C.†						R″ Obsd.	R″ Calcd.	Diff. in % Obsd.
28	40	2000	1.328	1.045	1.315	1.841	1.873	1.7
35	80	2000	2.640	1.318	-----	3.699	3.728	.8
Part D.‡								
46	40	2000	1.591	1.408	1.760	1.973	1.968	.1
47	80	2000	3.117	1.736	-----	3.938	3.923	.4

Note—* $2^{\frac{1}{2}} = 1.26$. With the same volume, agitation, etc., the K for an amount of 40 g. should be 1.26 times the K for 20 g. provided there is no piling effect. † Part C. A different sample of salt and but a single run. Agitator 1″ ×4.25″. Speed 298 r.p.m. ‡ Part D. A 4-6 mesh cut of salt from a different company (I. C.). Agitator same as in Part C but running at 240 r.p.m.

Several things are shown by the results of these experiments. With 80 g. of salt the piling effect of its volume became noticeable especially if the intensity of the agitation was low as it was in Parts A and B. With higher intensities of agitation as in Parts C and D the effect of this larger amount was lowered and almost disappeared. For the amounts of 40 g. and less in Part A there was no piling effect.

Part D shows the results from the use of a smaller particle salt with different shape characteristics which had been obtained from a different company. In Parts C and D the concentrations for the second minute are shown for comparison with those calculated by means of the equation from the values observed for the first minute, showing the normal operation of the law in both cases.

11. Size of the Particles.

One of the hypotheses upon which the Cube Root Law is based is that if two particles of the same material are geometrically similar, their surfaces, s_1 and s_2 are to each other as the two-thirds powers of their respective weights, w_1 and w_2. Therefore, with equal weights of two different sized particles of similar shape, it is easily shown that the total surfaces, S_1 and S_2, are to each other as the cube roots of the respective numbers of particles in each lot. Thus:

$$\frac{S_1}{S_2} = \frac{n_1 s_1}{n_2 s_2} = \frac{n_1 w_1^{\frac{2}{3}}}{n_2 w_2^{\frac{2}{3}}}$$, but since $n_1 w_1 = n_2 w_2$, we obtain

Eq. (12) $$\frac{S_1}{S_2} = \frac{n_1 \cdot n_2^{\frac{2}{3}}}{n_2 \cdot n_1^{\frac{2}{3}}} = \frac{n_1^{\frac{1}{3}}}{n_2^{\frac{1}{3}}}.$$

These equations are, of course only strictly true for the ideal case but it will be shown that they are quite closely approached in the actual case due to the statistical averaging effect of which mention has been made before. Where these two lots are being dissolved with other conditions the same, this is the ratio of the total surfaces at the commencement of the dissolution. Since it is possible to compare the rates at which the respective dissolutions are taking place, this gives a means of comparing the total surfaces of two lots of different sized particles.

The value of the initial rate (I.R.) in each case can be obtained by substituting in the equation for the velocity, Eq. (7), p. 34.

Eq. (13) $$\frac{dw_o}{dt_o} = \text{I.R.} = -3Kw_o^{\frac{2}{3}}.$$

Since the value of w_o is the same for each lot the ratio of their respective initial rates is the same as the ratio of their constants K. Combining the two equations and assuming that the initial rates are proportional to their respective surfaces, the resulting equation gives the relation desired.

Eq. (14) $$\frac{K_1}{K_2} = \frac{n_1^{\frac{1}{3}}}{n_2^{\frac{1}{3}}} = \frac{S_1}{S_2}.$$

The results given below show how closely this relation may be expected to hold.

TABLE 44.

Particle Size and Rate of Solution (1).

Expt. No.	Grams of Salt	Kind of Salt	R.P.M.	n_1, n_2	K_1 Eq.(8)	$\frac{K(4\text{-}6)}{K(3\text{-}4)}$	$\frac{n_1^{\frac{1}{3}}}{n_2^{\frac{1}{3}}}$
46d	40	4-6 I.C.	296†	482	1.560		
44a	40	3-4 I.C.	296	196	1.057	1.47	1.350

47c	80	4-6 I.C.	242	964	1.736		
47b	80	3-4 I.C.	242	392	1.209	1.43	1.350
131a	5	4-6 F.S.	Tumbler	62	.2314		
131b	5	3-4 F.S.	Type*	21	.1656	1.40	1.435

Note—* Reported in full on p. 59. The constants in Expts. 46-47 were calculated from the values of R′. In the tumbler experiments the particles were counted but in the others the numbers were taken from the averages.

† Free rotational agitations using the standard set-up.

In the above experiments, with the exception of Expt. 131, the Ks are single values obtained from the dissolution for the first minute. However, in the next table experiments are shown in which the determination of several values of the constant permits the use of a mean value which is more reliable.

TABLE 45.

Particle Size and Rate of Solution (2).

Expt. No.	Kind of Salt	K_1 Values	Sec.	Ave. K_1	$\frac{K(4\text{-}6)}{K(3\text{-}4)}$	$\frac{n_1^{1/6}}{n_2^{1/6}}$
		.01642	30			
50a	3-4 I.C.	.01698	60	.0167		
		.01837	10			
		.02341	30			
50b	4-6 I.C.	.02482	60	.0222	1.33	1.35
		.01669	20			
		.01679	40			
		.01750	60			
49a	3-4 I.C.	.01786	80	.01721		
		.02214	20			
		.02286	40			
		.02345	60			
49b	4-6 I.C.	.02438	80	.02320	1.35	1.35

Note—All agitations in Table 45 were standard, using 40 g. of salt and running at 240 r.p.m. The percentages dissolved in all of these cases were from 60-90%.

By using the value of the constant obtained over a considerable range of dissolution, the effects of irregularities in the dissolution action near the beginning are avoided. Attention is di-

rected to the very satisfactory agreement between the theoretical and observed values showing the extent to which reliance may be placed in Eq. 14.

12. Size Distribution.

When the particles used are not very close to each other in size the tendency at the beginning is to average these differences and show a mean value for the constant up to the time that the smaller particles begin to disappear. The rate then slows down to approach that of the larger particles that remain which it follows until they too begin to disappear. In a screen cut of the nature which we have been using the particles never disappear all at the same time. Some of these facts are shown in the table given below.

Conditions—This run was made on a mixture of 25 g. of fine dairy salt (almost 80% by weight was a 40-60 mesh T.S. cut) and 15 g. of a 3-4 mesh T.S. cut from the usual sources. It was a standard agitation and ran at 240 r.p.m.

TABLE 46. EXPT. 54.

Size Distribution. Mixture of Fine and Coarse Salt.

Time Sec.	Δt Sec.	c_1 g.	% Diss'd.	$c_1^{1/3}$	K_{30} Eq.(8)
0	0	39.80	0.0	3.414	—
30	30	10.75	73.0	2.207	1.207
90	60	2.85	92.5	1.417	.395

Note—Practically all of the fine salt was dissolved at the end of the first 30 sec.

The rapid disappearance of so many of the particles is reflected in the value of the constant. This is, of course, an extreme case and the grading action of the dissolution is very marked. As the particles were here grouped into two very distinct classifications of size ranges the change was necessarily quite abrupt. Usually this is not the case but it is very probable that more or less of this type of action takes place in most all cases where the size distribution is not so well identified as it is here. The next experiment illustrates this point.

Expt. 52. Run of Bag.

Conditions—Starting with a sufficiently large amount of the salt as received in the bag, four carefully-selected 40 g. samples were obtained by the quartering method. These samples represented a size gradation which was reported by the screen analysis of this material on p. 80. They were used in an equal number of runs with the usual standard agitation at 240 r.p.m. The averaged results are given below.

TABLE 47. EXPT. 52.

Size Distribution. Run of Bag.

Time Sec.	Δt Sec.	c g.	% Diss'd.	$c^{1/3}$	K_{30} Eq.(8)
0	0	39.56	0.0	3.408	----
30	30	22.83	42.3	2.837	.571
60	30	11.80	70.0	2.276	.561
90	30	5.78	85.5	1.795	.481
120	30	2.59	93.5	1.373	.422

Since over 80% of this material is larger than six mesh, the change is not so abrupt as in the previous example but the gradual decrease in the value of the constants shows the effect of the continual disappearance of the particles throughout the course of the dissolution. Therefore, the constants in this experiment can only be regarded as highly averaged values which represent the generalized rate changes that are occurring for the entire aggregate of solid regardless of its particular size distribution.

13. Layer Effects.

Several cases of agitation having an extremely low intensity were examined and it was discovered that this region was replete with some very interesting phenomena. No experiments will be given but a few of the characteristics may be commented upon. Using a tall, narrow tube with the salt at the bottom and a small and very slowly rotating agitator set midway up the tube, it was found that different layers of solution were formed which had very sharply defined concentration boundaries. It was also found that the manner in which the concentration changed at the top was no longer subject to any known laws and appeared to have nothing but an empirical basis. For instance,, the concentration at the top seemed to have a tendency towards linearity with time,

some experiments appearing over a 5-10 hour range to give a fairly good straight-line relation. Concerning the layers mentioned above, one case may be noted about a layer for which the following data were collected. A sample taken 5 mm. above the layer had a concentration of $R = 1.85$ while a sample taken 5 mm. below had one of $R = 24.54$, giving a very high concentration gradient of 22.69 g. of salt per 100 g. of water per cm. Other layers of obviously different concentrations could be simultaneously observed at various heights in the tube. These layers formed very rapidly after the agitation was started and changed their positions very slowly as the time went on.

14. Precision.

Due to the fact that there is a considerable variation in particle size even in a narrow screen cut, the fact that any constancy in results is obtainable at all is really quite surprising. The variance in shape is also a very disturbing factor as has been repeatedly emphasized. The possibility that a generalization can be made over a range of 50% dissolved must be laid to the statistical averaging effect of the large number of particles taking part in the reaction. If, in addition to these stabilizing influences, the mean effect of repeated runs on different samples is included, the averaging factor is made still more prominent.

After a suitable technique has been acquired, the values of concentrations obtained on duplicate runs may be expected to check to less than one per cent and often to one and two parts per thousand. With very low concentrations in the case of low intensity and poor distribution, especially of the N.F. regime, a large departure from this precision is expected and encountered. The reasons for this have been stated before. In these cases all that can be done is to make a large enough number of runs so that the average result will represent in a general way the order of intensity to which the agitation belongs.

LARGER SCALE EXPERIMENTS.

A few experiments were made in larger equipment in order to ascertain if the operation of the law took place in the same manner as it did in the laboratory. On account of the higher peri-

pheral velocities, one can not expect that those factors which had only a small effect on the small scale will remain equally ineffective on the larger scale. Some of these disturbing factors are such things as small irregularities of construction in the equipment, surface roughness and uncontrollable speed variations in the agitator.

1. Equipment.

The container used was an open wooden tank, 44″ deep with a diameter of 49.5″ at the bottom and 46.75″ at the top, having a capacity of approximately 3000 lbs. of water or about 350 gals. It was fitted with a straight paddle agitator consisting of a 3″ square wooden shaft the bottom of which was 7.5″ from the floor of the tank. At a distance of 2.75″ from the bottom of the shaft, a board 1″ thick by 3″ wide and 34.5″ in length passed through the shaft forming the agitator blades. Its edges had been considerably rounded off by long use. The agitator was driven by a motor connected to it by means of belts, shaft and gears. Two speeds were obtainable, 35 and 70 r.p.m. 2000 lbs. of water were weighed into the tank in 400 lb. lots. This amount (2000 lbs.) gave a depth of 30.6″ without the agitator going. The salt used was obtained by hand screening five one-hundred pound bags of the same kind of salt that had been used in the laboratory. It was presented to the screen for one time only and the cut taken was the 4 mesh T.S. oversize which thus differed from the laboratory material in containing the 3 mesh oversize fraction. 40 lbs. were used in each run. The first few runs were made in order to establish the proper time intervals needed to take the samples before all of the salt had dissolved. With both speeds the flow was that of the C.F. regime. Samples of 800 cc. each were taken in the same relative position as in the standard laboratory agitations and they were immediately bottled and set away for analysis. The constants for the plant equipment were found to be of the same order as those obtained in the laboratory and the results of several of these runs will be given to show how the increase in volume of over 450 times affects the character of the results.

TABLE 48. EXPT. 153.

Plant Slow—35 R.P.M. The Cube Root Law (1).

Time Min.	Δt Min.	c* g.	% Diss'd.	$c^{1/3}$	K_1 Eq.(8)
0.0	0.0	1.9690	0.0	1.2534	———
0.5	.5	1.8541	5.3	1.2285	.0498†
1.0	.5	1.6035	18.6	1.1704	.1162
1.5	.5	1.3790	30.0	1.1130	.1148
2.0	.5	1.1983	39.0	1.0621	.1018
3.0	1.0	.8873	55.0	.9609	.1012
4.0	1.0	.6612	66.5	.8711	.0898†

Mean († omitted) = .1085
Ave. D/M = 6.4%

Note—* Weight calculated from the concentration and divided by 20.

TABLE 49. EXPT. 160.

Plant Fast—70 R.P.M. The Cube Root Law (2).

Time Sec.	Δt Sec.	c g.	% Diss'd.	$c^{1/3}$	K_{15} Eq.(8)
0	0	1.9780	0.0	1.2553	-------
15	15	1.8524	6.3	1.2281	.0273*
30	15	1.6765	15.4	1.1880	.0401
45	15	1.4725	25.6	1.1377	.0503
60	15	1.3109	33.9	1.0944	.0433
75	15	1.1627	41.3	1.0515	.0429
90	15	1.0146	48.7	1.0048	.0467
105	15	.8802	55.7	.9584	.0464
120	15	.7653	62.0	.9147	.0437

Mean (* omitted) = .0447
Ave. D/M = 5.8%

Note—K_1 = .1791

It is at once apparent that irregularities are considerably more prevalent than with the smaller apparatus and that one cannot expect the same degree of exactitude. Possibly some of this is due to the wider screen cut that was used. An examination of the constants also shows that there is an interval at the beginning where often as much as half a minute is required before the flow of dissolved solid into the upper part of the tank has acquired a regulated character. Several other runs were made from

which the value of the ruling constant over a range of approximately 50% is taken to represent the constant for that agitation. Some of these are tabulated in the next section.

2. Study of Variables.

A comparison of the agitations at 35 and 70 r.p.m. was possible in the larger equipment. Additional runs were therefore made to obtain average values for the constants. The insertion of a baffle into the tank also permitted the study of another variable which had not been considered before. The plant runs were made with 40 lbs. of salt. The baffle consisted of a board 1″ thick and 3.5″ wide which was fastened in a vertical position to the wall of the tank and extended the entire depth of the tank. This acted as a breaker or baffle and changed the character of the agitation considerably as it broke up the vortex in the center from a 9.6″ to a 3.6″ drop from the still level of the water. The results are presented in a summarized form in the following table.

TABLE 50.

Variation in R.P.M. and Use of Baffle.

Expt. No.	Time Range Min.	% Diss'd. Range	K_1 Eq.(8)	Ave. K_1	T_{50}† Min. Ave.
35 R.P.M.					
153	0.5—3.0	5—55	.1085		
154	1.0—3.0	20—56	.1078	.1081	2.595
69 R.P.M.					
159	0.5—2.0	16—62	.1873		
160	.25—2.0	6—62	.1791	.1832	1.515
69 R.P.M. with Baffle					
164	.25—1.25	9—47	.2002	.2002	1.368

TABLE 51.

Ratios from Table 50.

Ratio of Agitations	Ratio of Constants	Ratio of Half-Times
$\frac{\text{Plant Fast}}{\text{Plant Slow}}$	$= \frac{.1832}{.1081} = 1.69$	$\frac{1.515}{2.595} = \frac{1}{1.71}$
$\frac{\text{Plant Fast (B)}}{\text{Plant Fast}}$	$= \frac{.2002}{.1832} = 1.10$	$\frac{1.368}{1.515} = \frac{1}{1.11}$

From the above results there are certain ratios that may be formed and these are shown in the next table.

Note—† The half-time values (T_{50}) are calculated in these cases by the use of Eq. (8) from the value of the single constant K within whose interval the 50% value of the concentration occurs. In this respect it is independent of any other portion of the dissolution and has required but two values of the concentration for its determination. The value of the time could, of course, be obtained graphically by plotting the concentrations directly against the times without assuming any kind of a law whatever and this is probably the only means when the agitation is extremely low.

3. Discussion.

The results obtained in the larger scale experiments show that the Cube Root Law governs the rate of dissolution in plant size equipment the same as it did in the laboratory apparatus. It is also shown that the study of agitation problems can be conducted in the plant equipment itself. This permits the collection of numerical data upon which definite conclusions may be based concerning the agitational value of changes that have been made in the equipment. For instance, in Table 51, the introduction of the baffle is shown to have increased the intensity of the agitation about ten per cent while in Table 50 the doubling of the stirrer speed increased almost seventy per cent.

In other words, it is possible to emphasize the fact that agitation as such, may now be thought of and discussed in quantitative terms. Since the establishment of a practical, numerical method of evaluating agitation was the stated problem of this research, it is believed that its solution has been satisfactorily accomplished.

SUMMARY.

1. The mathematical and physical research that has been done upon the motion of fluids has been examined and evaluated.

2. The qualitative characteristics of agitation have been analyzed.

3. The previous work by others upon agitation and the rate of dissolution of a solid in a liquid has been critically surveyed and correlated to that presented in this research.

4. A classification of agitation systems has been made and its use has been explained.

5. The various types of agitation have been listed and defined.

6. The factors affecting the dissolution of a solid and the intensity of agitation have been classified and described.

7. A general law concerning the rate of change of surface with time and concentration has been derived and the different special cases where it may appear have been considered and explained.

8. The Noyes-Whitney Law has been shown to be a special case of this law.

9. A general extension in meaning and application of the Cube Root Law has been postulated so as to apply in all chemical and physical transformations whose velocity is directly proportional to the first power of the interfacial contact surface.

10. This law has been experimentally verified throughout a wide variety of conditions in the study of heterogeneous reaction kinetics in the solid-liquid dissolution system.

11. Its experimental verification in the solid-gas system (naphthalene-air), has been made and certain variables have been studied therein.

12. The study of a solid-liquid chemical system (alum-aqueous ammonia), has been described in which the effect of protective coatings upon the operation of the law was satisfactorily explained.

13. The work of other investigators upon certain auto-catalytic reactions in solid-solid systems has been correlated to that contained herein.

14. The use of this law in the form of one of its special cases has been developed as a criterion of the intensity of agitation.

15. The idea of standard agitations of any type has been developed and a standard agitation has been set up for a particular type i. e. the free rotational type.

16. Certain regimes of flow which occur in this type of agitation have been described, named and studied.

17. Using the constants from the Cube Root Law as a cri-

terion, an extensive experimental study has been made in the salt-water dissolution system of a number of variables which affect the agitation of the free rotational type.

18. In connection with the study of the variables, several illustrations of the practical uses of this comparative method were disclosed.

19. The method of comparing the surfaces of irregular-shaped particles by means of their dissolution rates was shown theoretically and experimentally to be reduced to a simple comparison of their velocity constants as obtained by the use of the Cube Root Law.

20. Several of the properties of solid-liquid dissolution systems of extremely low intensities of agitation were described and attention was directed to the occurrence of layers, high concentration gradients, and certain other phenomena.

21. The experimental verification of the Cube Root Law on a larger scale was accomplished.

22. The large scale study of agitation variables was shown to be possible in the same manner that it was in the laboratory.

LITERATURE CITED.

[1] Wood. Whittemore and Badger, Chem. Met. Eng., **27,** 1176 (1922).

[2] Killefer, Ind. Eng. Chem., **15,** 144 (1923).

[3] Seymour, Agitating, Stirring and Kneading Machinery, Benn (1925).

[4] Euler, Hist. de l'Acad. de Berlin (1755).

[5] Lagrange, Oeuvres, **i,** 92, Paris (1867).

[6] Helmholtz, Phil. Mag., (4), **33,** 485 (1867).

[7] Mallock, Proc. Roy. Soc., (London), **45,** 126 (1888).
Couette, Ann. chim., **21,** 433 (1890).
G. I. Taylor, Phil. Trans., 223A, 289 (1922).

[8] Hele Shaw, Trans. Inst. Nav. Arch., **39,** 145 (1897); **40,** 21 (1898); **42,** 187 (1900).
De Villamil, Motion of Liquids, Spon (1914).
Reynolds, Papers, Cambridge (1901), **i,** 184; **ii,** 51, 153, 524, 535.

[9] Stanton, Phil. Trans., **214A,** 199 (1914).

[10] Gibson, Engineering (London), 117, 325 (1924).

[11] Lamb, Hydrodynamics. 5th Ed., Cambridge (1924), pp. 550, 631.

[12] Hill, Chem. Met. Eng., **28,** 1077 (1923).

[13] Murphee, Ind. Eng. Chem., **15,** 148 (1923).

[14] Roth, Z. physik. Chem., **110,** 57 (1924).

[15] Dodd, J. Phys. Chem., **31,** 1761 (1927).

[16] Milligan and Reid, Ind. Eng. Chem., **15,** 1048 (1923).

[17] Huber and Reid, Ind. Eng. Chem., **18,** 535 (1926).

[18] Witt, Ber., **26,** 1696 (1893).

[19] E. Brunner, Z. physik. Chem., **47,** 56 (1904).
Carlsen, J. chim. phys., **9,** 228 (1911).

[20] Wolff, Z. angew. Chem., **35,** 138 (1922).

[21] Van Name and Edgar, Z. physik. Chem., **73,** 97 (1910).

[22] Friend, J. Chem. Soc., **121,** 41 (1922).
Centnerzwer, Rec. trav. chim., **42,** 579 (1923).
Bekier, C. A., **22,** 1084 (1928).
Heller, C. A., **23,** 1804 (1929).

[23] Jablczynski, Z. physik. Chem., **64,** 748 (1908).

[24] Centnerzwer, (l.c.); Carlsen, (l.c.); Bekier, (l.c.).

[25] Wolff, (l.c.).
Wilderman, Phil. Mag., (6), **18,** 538 (1909).
[26] Stokes, Papers, Cambridge (1880), **i,** 1, 17, 75.
Lamb, Hydrodynamics, p. 628.
Reynolds, Papers, **ii,** 153.
Jeffreys, Phil. Mag., (6), **39,** 578 (1920).
Telfer, Trans. Inst. Nav. Arch., **69,** 174 (1927).
[27] Columbia University, Dept. Chem. Eng., Thesis, A. Cervi, (1923).
[28] Schurr, J. chim. phys., **2,** 245 (1904).
L. Brunner and Tolloczsko, Z. anorg. Chem., **56,** 58 (1908).
Gaillard, Compt. rend., **150,** 217 (1910).
Ritzel, C. A., **5,** 1385 (1911).
Le Blanc, C. A., **8,** 2288 (1914).
[29] Schurr, (l.c.).
[30] Van Name and Edgar, Am. Jour. Sci., (4), **29,** 237 (1910).
E. Brunner, (l.c.).
Eucken, Jette and La Mer, Fundamentals of Physical Chemistry. McGraw-Hill (1925), p. 442.
[31] Fick, Phil. Mag., (4), **10,** 30 (1855).
[32] Weber, Phil. Mag., (5), **8,** 487, 523 (1879).
[33] Noyes and Whitney, J. Am. Chem. Soc., **19,** 930 (1897).
[34] Brunner and Tolloczsko, Z. physik. Chem., **35,** 283 (1900) ; Z. anorg. Chem., **28,** 314 (1901) ; **35,** 23 (1903) ; **56,** 58 (1908).
[35] E. Brunner, (l.c.).
[36] Nernst, Z. physik. Chem., **47,** 52 (1904).
[37] Meyer, Z. Elektrochem., **15,** 249 (1909).
Roth, Z. Elektrochem., **15,** 328 (1909).
Denham, Z. physik. Chem., **72,** 641 (1910).
Hevesy, Z. physik. Chem., **89,** 294 (1914).
Collenberg, Z. physik. Chem., **101,** 117 (1922).
[38] Drucker, Z. physik. Chem., **36,** 173 (1901).
Auren, Z. anorg. Chem., **27,** 209 (1901) ; Z. physik. Chem., **45,** 182 (1903).
Van Name and Bosworth, Am. Jour. Sci., (4), **32,** 207 (1911).
Centnerzwer, Z. physik. Chem., **122,** 455 (1926) ; **137,** Abt. A, 352 (1928).
Straumanis, Z. physik. Chem., **129,** 370 (1927).
[39] Drucker, Z. physik. Chem., **36,** 693 (1901).

Centnerzwer, Z. physik. Chem., **87,** 692 (1914); **89,** 213 (1914); **131,** 214 (1928).

[40] Drucker, Z. physik. Chem., **36,** 173 (1901).
E. Brunner, Z. physik. Chem., **51,** 494 (1905).

[41] Marc, Z. physik. Chem., **61,** 385 (1908); **67,** 470 (1909); **68,** 104 (1909); **73,** 685 (1910); **75,** 710 (1911); **79,** 71 (1912); Z. Elektrochem., **15,** 679 (1909); **16,** 201 (1910).
Wagner, Z. physik. Chem., **71,** 401 (1910).
Le Blanc, Z. physik. Chem., **77,** 614 (1911); **86,** 334 (1913).
Fischer, Chem.-Ztg., **36,** 527 (1912).

[42] Jenkins, J. Am. Chem. Soc., **47,** 903 (1925).
McCabe, Ind. Eng. Chem., **21,** 30, 112 (1929).

[43] Wilderman, Report British Assoc., (1896), p. 751; Phil. Mag., (6), **2,** 50 (1901); (6), **4,** 270, 468 (1902); (6), **18,** 538 (1909); C. A., **3,** 2081 (1909).

[44] Langmuir, J. Am. Chem. Soc., **38,** 2221 (1916) and later papers.
Marcelin, Ann. phys., **3,** 127 (1915).

[45] Jablczynski, C. A., **21,** 3525 (1927); Z. anorg. allgem. Chem., **180,** 184 (1929).
Centnerzwer, Z. physik. Chem., **137,** Abt. A, 352 (1928); **141,** Abt. A, 167, 297 (1929).

[46] Jenkins, (l.c.).
Marc, Z. physik. Chem., **61,** 385 (1908) and later papers.
Le Blanc, Z. physik. Chem., **77,** 614 (1911).

[47] Walker, Lewis and McAdams, Prin. of Chem. Eng., McGraw-Hill (1927), Ch. 18.

[48] Roginskii, C. A., **24,** 1017 (1930); Z. physik. Chem., **138,** Abt. A, 21 (1928).

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